Commentary

ORGANIZATION OF RESEARCH

Two things have happened during the last month which make it more important than ever to think very seriously about the organization of research. The first is the publication of the annual report of the D.S.I.R., whose budget has increased from £36 million for the five-year period 1954–59 to £61 million for the period 1959–64, and the second is the 'consideration' that the Government is giving to a possible British satellite programme.

Scientific man-power and engineering skill are our national capital for we depend entirely on what we can earn by our industry and on what little remains of our investments. Man-power is limited and it is therefore very important that there should be a serious plan, not just a five-year plan but a plan for the next 15 or 25 years, to decide what the world is likely to require by the 1980s and how we can best direct our research effort to this end. It must be remembered that it takes at least ten years for the average project to travel from the research laboratory to large scale production.

In the United Kingdom there are four main bodies responsible for pure and applied research: the universities, the D.S.I.R., the Ministry of Supply on behalf of the Services (except the Admiralty) and industry. Each has a very definite and distinct part to play and, provided it is arranged that there is no overlap, the need for a single organizing body does not arise. The avoidance of overlap is not easy—and it is doubtful if it can be achieved in present practice—because the Ministry of Supply preserves many projects behind barbed wire and underneath red tape, projects that should be well known to other scientists to help them with their own work. Nor does there seem a real need for the Admiralty to undertake work that can be done by civilian authorities; they test their own model ships and even do their own research on semiconducting devices, subjects which are already being investigated by other research establishments.

The place of industry and the universities in this scheme of things is quite distinct. Industrial research is mainly, and indeed should be, applied research for industry is very prudent and wishes to see adequate returns for its investment. The universities are there to do fundamental research and to train scientists in the techniques of fundamental research. In this connection the new D.S.I.R. policy of giving universities long term grants for particular projects, up to a maximum of 17 years, and providing the universities with large pieces of equipment such as electron microscopes, bubble chambers and the like, is very welcome indeed. The universities badly need this equipment for from them should come our best scientists. The work of the D.S.I.R. is three-fold. It runs a number of research stations, it provides financial support for the research associations and supplies a large amount of the money for research at the universities. The first of these functions, the D.S.I.R.'s own stations, have had a thorough overhaul over the past year and various new policies have been implemented. These involved the reorganization of the National Physical and the National Chemical Laboratories and on the whole the changes appear to be beneficial. There still seems a considerable discrepancy in the expenditure of the various D.S.I.R. stations. At the present moment rather less is spent on the Mechanical Engineering Research Laboratory than on either the Building Research Station or the Road Research Laboratory. Building research is a very admirable project but should be financed to some considerable extent by the building industry whereas the fundamentals of mechanical engineering are absolutely necessary in order to 'provide industry with an adequate foundation for its own applied research and development'.

The D.S.I.R. quite rightly and properly wishes to persuade industry to bear more of the cost of the research associations and this is certainly a trend in the right direction. It is proposed that research associations should be encouraged to take a certain amount of sponsored research, up to about 15 per cent of their total effort, and this will enable small firms without facilities of their own to have specific projects done for them. One director of a research association put the other point of view: he pointed out that if a specific project is to be kept completely confidential what happens if a member firm then approaches the association on the same or a similar problem. Is the work to be repeated?

Cautious consideration should be given to the suggestion that Britain should enter the space race. One report quotes about a million dollars for a single solar battery! It is true that a great deal of prestige would be derived if the project were successful and it can also be argued that we would be sending military rockets up in any case. But the time has come to consider, not on political grounds but purely on a question of economic survival, as to whether we can afford to spend something of the order of ten times as much on defence research as on pure and applied research. The plea must be: more investigation into the returns that can be expected from research investment and, if necessary, even more 'direction' to avoid duplication and wastage of our resources.

47.3

FRICTION MATERIALS

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At one time simple blocks of wood, leather or metal were used to brake carts or carriages and railway trains still use cast iron blocks today. With the introduction of motor vehicles these were found to be inadequate and were replaced, first by woven cotton and later asbestos impregnated with organic materials. For the most severe application it has been found that even asbestos linings are inadequate and sintered metal or cermet friction materials must be used.

THE EARLIEST types of friction materials were blocks applied to tyres. These blocks were used on horse-drawn carts and carriages, on railway trains and on the first motorized vehicles. They were made of wood, preferably elm or poplar, of cast iron, leather, old rope or hair belting and in particular camel hair belting. (*Figure 1* shows the use of leather in the form of an old boot for braking a cart.) Such were the materials used for braking almost up to the end of the nineteenth century. With the advent of new products, these early types of brake block have gradually been replaced, but even today the majority of trains are still stopped by cast iron blocks applied to the steel tyres. Shortly before the turn of the century, as motor cars were beginning to appear, the need for more durable braking materials was real, but had not apparently been given much attention. Laminated rubber–canvas blocks were being made in France but these wore away very rapidly.

At about this time Herbert Frood of Manchester went to live at Combs near Chapel-en-le-Frith amongst the North Derbyshire hills. He was impressed by the difficulties which the carters had in bringing down their loads of limestone from the hill quarries and he applied his enquiring and inventive turn of mind to investigating the problems of braking and brake block manufacture. He was soon able to make and market in small quantities an oil-impregnated cotton textile material—and this was the beginning of the friction materials industry.

The first decade of the twentieth century saw the manufacture of friction linings impregnated with a variety of oily, gummy or resinous substances. These were reasonably effective and durable while speeds were low and brakes were large. During this period direct braking against the tyres was being replaced by drum braking, where the friction lining acts against the outside, or more usually the inside, of a steel or cast iron drum mounted on the wheel shaft. The first step in improving the heat resistance was to replace the cotton cloth by a woven asbestos fabric and this has been the basis of the major part of the friction materials made during the last half century. These materials have been made by impregnating woven asbestos with bitumens, oils, rosin, synthetic resins and rubbery compositions.

Since the second world war an increasing proportion of automotive brake linings have been made by moulding processes without using a textile fabric. More recently wholly inorganic materials have begun to be used for the severest duty applications. In these cases disc brakes are used in which the friction material is in the form of pads or buttons operating against the side of a steel disc. This design avoids the stresses which result in drum brakes from steep temperature gradients, and is widely used on aircraft and increasingly on the larger automobiles.

Asbestos Friction Materials

Asbestos is a generic term for several different fibrous silicate minerals. Chrysotile or white asbestos, $Mg_3Si_2O_5(OH)_4$ is the type mainly used in friction materials. It is an unique material in that whereas all other fibrous substances have a linear molecular structure, chrysotile has a basically laminar structure. The layers however are curved owing to the somewhat unequal spacing of the brucite $Mg(OH)_2$ and silicate Si_2O_5 layers which go to make up the chrysotile structure. The details of this interesting structure have been established by E. J. W. WHITTAKER[1]. The ultimate fibrils consist of thick walled tubes made up of some ten layers with an outside diameter of about 250Å and an inside diameter about half this. The core and spaces between these tubes are to a large extent filled with segments of the same material. *Figure 2* shows a specimen of asbestos-containing rock and a model of its molecular structure.

Figure 1. Some of the earliest type of friction materials made specifically for braking were blocks applied to horse drawn carts, but before this an old leather boot (as shown here) was often used

Chrysotile asbestos has the attractions of great tensile strength, flexibility and heat resistance. It is stable to over 600°C and when it does break down at higher temperatures, the silicates so formed remain as solids up to at least 1200°C. It has a high coefficient of friction but a poor resistance to wear and it must be combined with other materials to produce acceptable friction linings.

Woven Linings

In woven linings the strength is provided mainly by the woven asbestos, although this may be reinforced by included zinc or brass wires. These wires have the additional function of increasing the thermal conductivity and thus lowering the temperature of the lining surface and so reducing the rate of wear. As methods of weaving have improved the need for included metal wire to give adequate strength during weaving has disappeared but some 10 to 20 per cent of cotton or rayon is usually added for this purpose. Examples of woven brake linings are shown in *Figure 3*.

The ply-woven asbestos is impregnated with a bonding medium which serves greatly to reduce the rate of wear and is well chosen to give a uniform friction at any required level, with freedom from fade or fall in friction up to say 300°C. The bonding media fall into three groups: bitumens, asphalts and natural resins such as rosin; drying oils such as linseed, tung and dehydrated castor oil; and synthetic resins. Various combinations of these may be used. They are broadly suitable for progressively higher temperatures in the order shown. The bitumens are mainly used where speeds and therefore temperatures are low. They were suitable for early slow-moving road vehicles, but are now restricted to some of the heavier and slower moving industrial machines. Since these bonding agents are thermoplastic the friction falls or ' fades ' if the temperature becomes high enough to cause softening.

Drying oil bonding agents have the advantage that when polymerized by oxygen curing they are not thermoplastic and consequently they provide an effective bond at higher temperatures. Their fairly high viscosities necessitate vacuum impregnation, and the hardness of the linings after baking does not allow much adjustment of radius so that linings must be made specifically for the various sizes required.

Synthetic resins of the phenol formaldehyde type increase both the strength and the heat resistance of friction linings. The simple unmodified phenolic resins are not of much use as they are too hard and they give erratic friction. The more resilient oil-modified and oil-soluble types of phenolic resin give more uniform friction with less tendency for the friction to fall or fade at high temperatures. Such resinous impregnants may be made from substituted phenols, from cashew nut shell liquid or by modification with oils.

Moulded Linings

The use of synthetic resins as bonding agents eliminates the need for a strong woven fabric since these resins will bond even non-fibrous mineral particles together to give high strength plastics. Hence with these resins one can produce moulded linings by

a choice of wet and dry forming techniques. These permit the introduction of any desired solid powders to modify the friction and wear properties. Short fibre asbestos is effective in giving strength to the

Figure 2. Model of the crystal structure of chrysotile asbestos (× 150 million) with a specimen of asbestos-containing rock

moulded product, and is in fact advantageous in facilitating flow during forming operations as well as being much cheaper than the longer fibres which are needed for spinning. Thus moulded linings can be made from cheaper raw materials and can have a wider range of properties. On the other hand they are rigid and for drum brakes they must be made specifically for every drum size whereas woven linings can be made flexible, and so are readily adaptable for use in various sized drums. *Figure 4* shows one type of moulded brake lining containing chopped asbestos yarn.

A typical moulded lining will be made from a mixture of short fibre asbestos, oil-modified phenol formaldehyde resin, pre-cured resin powder, inert mineral fillers with smaller amounts of lubricants, graphite, metal particles and selected friction modifiers. These are mixed either dry or in the presence of solvent which is subsequently dried off. The mix is then moulded in a positive mould under conditions similar to those used for moulding other thermosetting resin materials or the mix may be preformed and partly cured in rectangular strip form after which it is quickly heated to a higher temperature and bent to the required radius of curvature round a former with final cure in ovens. Many variants of these techniques may be used depending on the size, shape, quantity and type of linings being made.

Another type of moulded friction lining is made in roll form as flexible strip by bonding short fibre asbestos and other fillers with rubber, a synthetic rubber-like polymer or a polymerized drying oil. This type of moulded product has the same dimensional adaptability as rolls of woven material.

Yet further types of organic bonded friction materials are more particularly suited to clutches and automatic transmission systems than to brakes. These include asbestos millboard or felted asbestos made on a paper making machine and bonded with a synthetic resin, and asbestos yarn coated with a rubber-based compositions wound on to a mandrel or chopped and moulded to form an annular shaped clutch facing.

Research and Development

We have now outlined the main types of asbestos-based friction materials and we must consider what developments are taking place. Brake linings require to have:

(*i*) An appropriate coefficient of friction for the particular design of brake.
(*ii*) A uniform coefficient of friction over a wide range of temperature, so that 'fade' or fall in performance of the brake does not occur under severe conditions of usage.
(*iii*) A low wear rate.
(*iv*) Good water resistance and quick recovery of frictional performance after immersion in water.
(*v*) Freedom from noise.

Figure 3. Some examples of woven brake linings. Woven linings are made of asbestos reinforced with 10 to 20 per cent cotton or rayon, or in some cases with fine zinc or brass wires woven in with the asbestos

(*vi*) Resistance to oil.
(*vii*) Adequate mechanical strength.
(*viii*) Absence of abrasive action on the brake drum or disc.
(*ix*) Good bonding properties to facilitate attachment to the brake shoe backing member.
(*x*) Freedom from sensitivity to humidity which can cause 'early morning sharpness' or excessively high friction after standing.

Figure 4. Moulded brake lining containing chopped asbestos yarn

These are perhaps the most important requirements from brake linings but the list could be extended by such items as absence of smell, freedom from shrinkage or swelling, absence of ageing or deterioration either after fitting or during storage, and low cost.

Some brake systems have a marked servo effect whereby the braking force is increased in proportion to the frictional force. This permits the use of low friction linings but exaggerates the effects of any variability in friction. Brake design in this country is beginning to favour the use of reduced servo or non-servo systems for higher powered cars whereby greater stability can be obtained but high friction is desirable.

Heat Resistance in Friction Linings

Current trends in vehicle design and operation greatly accentuate the importance of heat resistance in friction linings. Higher speeds, with the energy dissipated increasing as the square of the speed, smaller wheels and minimum unsprung weight required for obtaining a smooth ride, and greater shrouding required for streamlining and ascetic reasons, have all contributed to increase the temperature at which brake-linings must operate.

It has been shown[2] that the energy dissipated at the brakes of a car is related to the mean journey speed when other factors are kept constant. For a particular car and route but with different drivers, it was found that this energy increases as the $3{\cdot}4^{th}$ power of the mean journey speed. Typical drum or lining surface temperatures are around 100°C in general use, 250°C after a long steep hill, and 400°C after the heavy braking which causes fade, although much higher temperatures such as 500°C, 600°C or more may easily be produced in some cars by hard braking. The instantaneous temperatures at the real points of contact during a braking application are much higher still. For measurement of these transient temperatures a very quick response is essential and R. C. PARKER and P. R. MARSHALL[3] have developed the lead sulphide cell with a response time of 10^{-4} seconds for this purpose. Calculations of the heat transfer by T. P. NEWCOMB[4] have shown good agreement with experimental measurements. *Figure 5* shows disc brake temperatures on a dynamometer being measured with a thermocouple.

The temperature rise at the lining surface during single stops from 30 m.p.h. in five seconds with drum brakes, and from 90 m.p.h. in ten seconds with disc brakes is shown in *Figure 6*. These data were obtained with a detector having a response time of about one tenth of a second. These temperatures are astonishingly high for organic materials and in no other application are organic polymers expected to withstand such severe conditions except in rocket engines for guided missiles. Clearly incipient degradation must occur since most polymers breakdown rapidly between 400° and 500°C if not before.

Figure 5. Measurement of disc brake temperatures on dynamometer using a thermocouple

The nature of the high temperature changes in resins are therefore important including the amount of breakdown under given conditions, the effect of stabilizers and the nature of the residue when partial degradation has occurred. This last is of importance as the actual working surface of a brake lining is often made up of such degradation products. This

type of work involves techniques like infra-red spectroscopy, gas chromatography and x-ray diffraction for studying the materials in the interface, photoconductive cell measurement of instantaneous temperatures, and the damping of ultrasonic waves for measuring changes in physical properties.

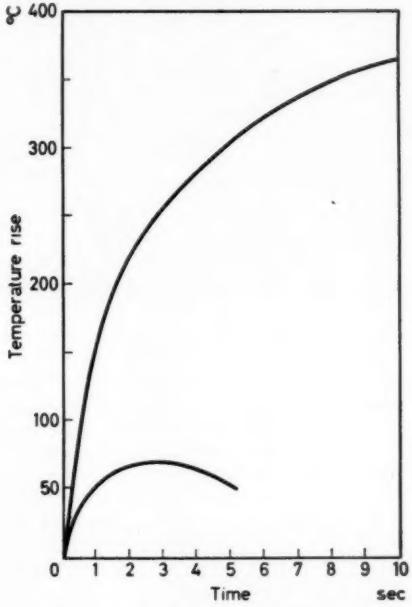

Figure 6. Temperature rise during single stops from 30 m.p.h. in 5 sec and 90 m.p.h. in 10 sec

General Trends

In this sort of way the early empirical development of brake linings is beginning to be explained in terms of fundamental laws. However the ability to correlate a particular structure with friction and wear behaviour is still in the future. What can be done at present is to correlate some of the required characteristics with simpler properties, so that if they cannot be expressed in terms of actual molecular structures they can at least be specified in a useful manner.

Some of the above list of requirements for brake linings also apply to clutch facings, but here there are some additional needs such as smooth take-up, absence of judder and freedom from sticking on storage in the clamped position. Durability is particularly important in clutch facings because replacement of a clutch facing usually involves removal of the engine of a car.

Sintered Friction Materials

For the most severe duties organic bonded friction materials are inadequate. This arises either where the temperatures are extremely high because of high speeds as in aircraft brakes or because of heavy duties at lower speeds as in clutches for earth moving equipment and the like.

Sintering techniques permit the fabrication of metal-based materials containing components which could not be included in castings such as incompatible metals, graphite, molybdenum disulphide, oxides, in fact any stable inorganic materials. The essentials for the process are fine irregular shaped particles which are well mixed together, compacted at a pressure of around 10 to 25 tons/in², sintered at about 800°C for copper-based materials and at rather higher temperatures, some 1050°C, for iron-based mixes. The materials are finished to size by machining.

Metal Friction Materials

The copper-based sintered metal friction materials consist predominantly of copper which has good heat resistance and high thermal conductivity. This latter factor helps to keep down the maximum temperature at the rubbing surface by permitting the heat to be conducted away through the friction material as well as through the mating surface, but may involve some redesign of the brake mechanism to prevent this heat raising the temperature of the hydraulic fluid in the actuating system above its

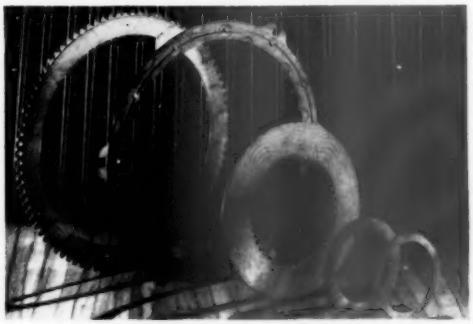

Figure 7. Samples of sintered metal facings for clutches and automatic transmission systems

boiling point. A few per cent of tin are added to convert the copper into a bronze, so increasing the strength and wear resistance of the matrix. A similar quantity of lead acts as a lubricant during forming and gives smooth engagement. Graphite and molybdenum disulphide are often added for the

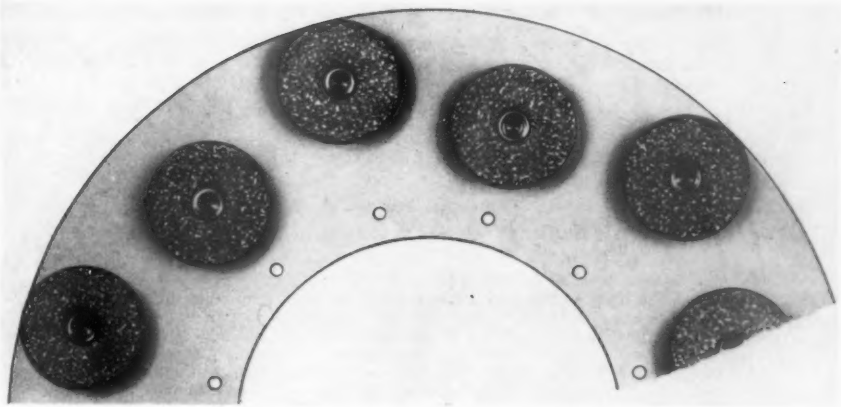

Figure 8. Ferodo cermet friction pads formed in steel cups and riveted to a supporting member. These cermet friction materials can withstand very high temperatures and are therefore used in such applications as the braking of jet aircraft

same reasons. Iron is added to raise the friction and by its scouring action to prevent seizing. Silica is added for similar reasons. Products of this type are mainly used as clutch facings particularly in heavy earth moving equipment and in automatic transmission systems (*Figure 7*). Their extremely low rates of wear are a great asset in these applications, and are essential in electromagnetic brakes and clutches where wear alters the clamping force.

Cermet Friction Materials

Whilst these sintered metal products have outstanding wear resistance at moderate temperatures, they have a low friction and only extend the temperature range of friction materials a little above that of the organic types. For the highest temperatures cermets must be used. These contain approximately equal volumes of a metal phase and a ceramic phase. One or other or both may form a continuous network, the second phase being in some cases in the form of discrete particles in a continuous matrix. The ceramic phase is typically silica, alumina, or mullite, but many other components may be included. Depending on the particular components used, the cermet may be simply a mechanical mixture or there may be solution or chemical interaction between the metal and ceramic components.

Cermet friction materials have generally less strength than sintered metals and require a supporting metal cup. They have a high stable friction and low wear rate. Their high thermal conductivity again permits them to function as an additional heat sink, while their general heat resistance and tolerance of severe thermal stress are outstanding. They can therefore function at temperatures up to 800 to 1000°C and even higher. They are pre-eminently suitable for braking jet aircraft with their high landing speeds, but they are also finding many applications in high duty industrial braking (*Figure 8*).

As so often happens, technology in this rather specialized industry is producing new materials to meet the changed requirements of this age of speed.

The author wishes to thank the Directors of Ferodo Limited for permission to publish this paper.

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X-RAY FLUORESCENCE SPECTROSCOPY

Applications of a Simple Apparatus using Radioactive Sources

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Conventional x-ray fluorescence spectroscopy employs an x-ray tube as a source of x-rays and a diffracting crystal spectrometer to analyse the fluorescent x-rays produced in the sample. A simple apparatus for this kind of work can be constructed by substituting a radioactive source for the x-ray tube and a proportional or scintillation counter for the crystal spectrometer. The apparatus is well suited to work of a simple and routine kind, such as the determination of metal plating thickness, or the determination of molybdenum in steel samples.

X-RAY fluorescence spectroscopy is similar in principle to visible and ultra-violet emission spectroscopy, in that electrons in atoms of the samples under investigation are excited from their normal states, and the reorganization that then takes place in the excited atoms results in the emission of radiation. This radiation is characteristic of the material being examined, and these spectrographic methods have become valuable tools for qualitative and quantitative analysis.

In the simple picture of the atom due to Bohr, the atom consists of a central nucleus surrounded by shells of electrons at different distances from it, the electrons in different shells possessing different amounts of binding energy. It is electron jumps between these shells that give rise to the phenomena of emission spectroscopy; transitions between the outer, loosely bound shells give visible or ultra-violet light, and transitions between the inner, tightly bound shells give rise to x-rays. For instance, the characteristic yellow light of a sodium discharge lamp is due to transitions between the outer shells of the sodium atom, and consists of two spectral lines of wavelength about 5900Å. While the x-ray emitted from tungsten when an electron falls to the innermost *K* shell from the adjacent *L* shell has a wavelength of 0·21Å.

X-rays are usually described in terms of the energy of their quanta, measured in electron-volts, rather than in terms of their wavelengths. Thus the energy of the tungsten x-ray mentioned above is 58 keV, the energy and wavelength of x-rays being related by the equation

$$\text{Energy (in keV)} = 12{\cdot}4/\text{Wavelength (in Å)}.$$

Although there is no difference in principle between the different branches of emission spectroscopy, x-ray spectroscopy appears in practice almost a different subject, owing to substantial differences in the kinds of spectra produced and the experimental techniques used.

Form of X-ray Spectra

The electrons in any one shell do differ slightly from each other in energy, and in the loosely bound outer shells of the heavier elements, which contain many electrons, these differences can become comparable with the difference of energy between adjacent shells. Thus the visible spectra due to transitions between outer shells can become very complex, because of the large number of possible transitions of closely similar energy. X-ray spectra do not show much complexity, for every element, except hydrogen, has only two electrons in its first (*K*) shell and the differences of energy between electrons in one shell are small compared with x-ray energies. With simple methods of detection the *L*–*K* transition in a particular element is observed to give monochromatic radiation energy of about 10·25 $(Z-1)^2$ electron volts, where Z is the atomic number of the element. The great simplicity of the x-ray spectra is one of their great differences from visible and ultra-violet spectra; it is one of the important advantages of this type of spectroscopy.

Experimental Methods

How are these spectra excited, and how are the excited emission spectra recorded? In the standard x-ray spectrometer the spectra are excited by rays from an x-ray tube; these x-rays must be of higher energy than the fluorescent x-rays that are to be excited.

X-rays whose energies are of about the same order as those of *L*–*K* transitions (0·1 to 100 keV) are

absorbed in matter almost entirely by the photo-electric effect which is just the process the spectroscopist needs for exciting the spectra he wants. In this process the incident, exciting x-ray photon can be thought of as colliding with and being absorbed

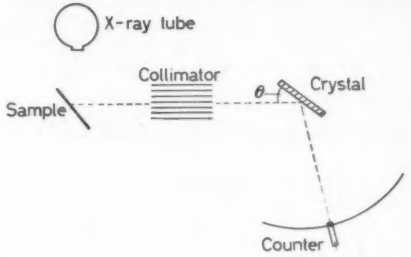

Figure 1. Schematic diagram of x-ray spectrometer

by an electron of an atom in the sample. The excess energy given to this electron allows it to escape from the atom and the vacancy thus caused in one electron shell is filled by another electron from a shell further out from the nucleus, and this is accompanied by the emission of x-radiation.

The emitted radiation will consist of a mixture of x-rays characteristic of each of the elements which compose it, and for identification and measurement of these components the radiation must be analysed into its separate spectral lines. This can be done by means of a diffracting crystal mounted on a turntable, with a Geiger or proportional counter also mounted to rotate so that when the crystal turns through any angle the counter turns through twice that angle (see *Figure 1*). X-rays of different energy will be diffracted strongly, ' reflected ' at different values of θ, and the angle at which this occurs for a particular x-ray is known as the Bragg angle. Whenever this angle corresponds to the Bragg angle for ' reflection ' for one of the x-rays emitted, these x-rays will register in the counter, so that the constituents of the mixture can be recognized and determined from the series of peaks obtained on a graph of counts per second against crystal angle, plotted on a recorder.

While this basic idea was well known as long ago as 1932 there have been two recent developments which have stimulated interest in this subject: the development of electronic counters for atomic energy work which can be used for recording these spectra—and this is greatly preferable to the original method of recording on film—and advances in electronics have improved the stabilization of the output of x-ray tubes.

Radioactive Source Method

In the type of spectroscopy under discussion both the x-ray tube and the crystal spectrometer are omitted. Instead of the tube, which may give an output corresponding to 10^4 to 10^6 curies of radioactivity, a radioactive source of about 100 microcuries is used. (A curie is a measure of radioactivity, equal to $3{\cdot}7 \times 10^{10}$ radioactive disintegrations per second.) Instead of a crystal spectrometer to resolve the mixture of x-rays, this is done by using the capacity of a proportional counter to discriminate between x-rays of different energy. The great difference in source strength between the two methods is largely due to the fact that the total path length from source to the counter can be cut from one to two feet to about one inch. Also in order to efficiently resolve x-rays by using their different Bragg angles a high degree of collimation is necessary but this is not so when they are resolved on the basis of their different energies.

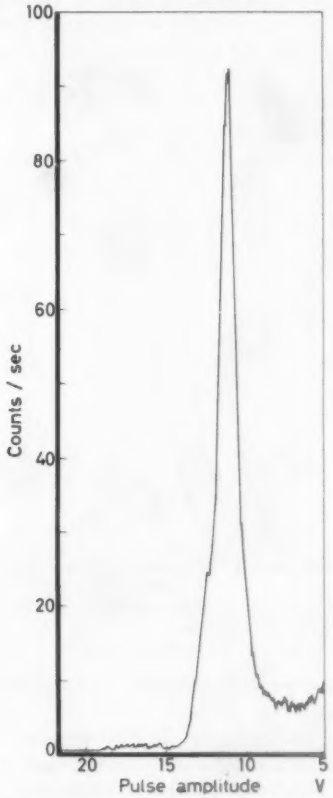

Figure 2. X-ray peak from barium in solution

Against the gain in simplicity of this system must be set the fact that the resolution of the proportional counter is not nearly as good as that of the crystal spectrometer, and this sets very severe limits on the radioactive source method.

The Proportional Counter

The x-ray proportional counter generally consists simply of a metal tube, with a thin wire running down the centre, which is electrically insulated from the sides. This tube has a window of thin plastic foil, or beryllium, at the midpoint of its length, and is filled with a suitable counting gas, such as a mixture of 90 per cent argon and ten per cent methane. When the central wire is held at a high potential, around 2000 volts, x-rays entering the counter produce electronic voltage pulses, and the energy of these pulses is proportional to the energy of the original x-ray.

These pulses are amplified electronically and passed through a pulse analyser, or kicksorter, and a recorder trace is finally obtained which is a direct representation of the spectrum of radiation entering the counter, being a graph of counts per second against energy. In the case of a monochromatic source the graph will consist of a single peak, such as the trace reproduced in *Figure 2*.

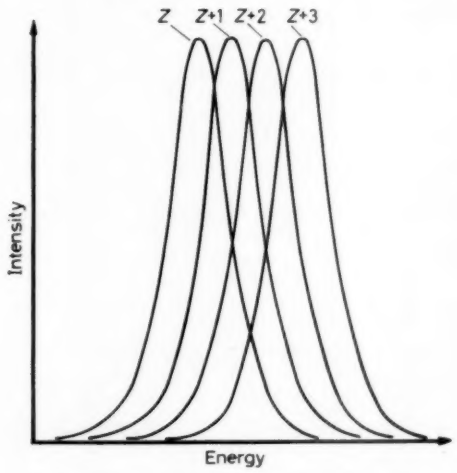

Figure 3. Overlap of x-ray peaks from adjacent elements in a proportional counter

The x-ray energies of L–K transitions are a smooth function of atomic number and the most difficult task will be to resolve x-rays from elements differing by one unit of atomic number, *e.g.*, iron and cobalt or potassium and calcium. Unfortunately, even a theoretically perfect counter will not resolve these rays, the separation of the Gaussian peaks obtained from the pure elements being both in theory and practice approximately equal to half the width of the peaks measured at half their heights (see *Figure 3*). The overlap at a given peak of an element separated by two units of atomic number is about five per cent; for an element separated by three units of atomic number the overlap is less than one per cent.

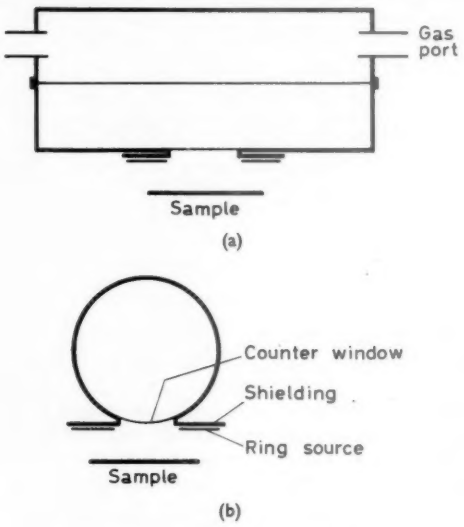

Figure 4. (a) Arrangement of the apparatus for a proportional couhter and (b) section of the apparatus

In spite of these limitations the results, as outlined below, indicate that this simple method of x-ray fluorescence analysis has considerable possibilities, particularly for routine examination of fairly simple systems.

Measurement of the Spectra

The five examples which are reported here are drawn, as far as possible, from different fields of study, to give an idea of the scope of the method.

Electroplated Layers—The apparatus for the measurement of the thickness of plated layers is shown in *Figure 4* and the results given (*Figure 5*) are for chromium plate on a nickel backing.

The source was mounted as an annulus round the counter window so that no direct radiation entered the window, and consisted of tritium H^3,

absorbed on zirconium metal. This is a convenient method for preparing stable sources of tritium. With sources of higher energy radiation, a few millimetres of lead shielding are required to prevent direct radiation from penetrating the counter wall and so flooding the counter with unwanted pulses. This type of experimental arrangement was used for all the results reported here, but the source shape was not always an annulus.

Figure 6 shows a typical recorder trace from one sample of chromium plate. The chromium x-ray peak

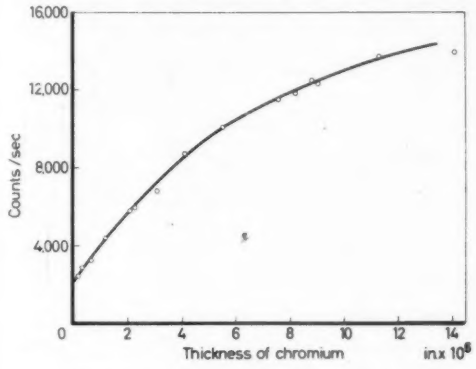

Figure 5. Measurement of chromium plate thickness using a tritium source

and that from the nickel backing can both be seen; the resolution of the counter was such that there was negligible overlap of the peaks, at the peak maxima. The potentialities of this apparatus for continuous plating thickness measurement are good and at the present time the conventional x-ray spectrometer is just beginning to be used for process control in tin plate manufacture. The industrial method of measuring chromium plate thicknesses has often been hydrochloric acid and a stop-watch, the time being noted for the acid to penetrate to the nickel layer underneath!

Solution Strengths—The accuracy obtainable in measuring the strengths of barium solutions with a source of 60 microcuries of tungsten 181 is shown in *Figure 7*. The curves drawn are 95 per cent confidence limits, based on the scatter of the experimental points shown; 20,000 counts were taken for each measurement which only required five minutes counting time with the one per cent solution, and correspondingly less as the solution strength increased. *Figure 2* shows a barium x-ray peak from a barium solution.

Paint Films—A curve drawn from measurements of the thickness of films of titanium dioxide, a widely used paint pigment, with caesium 131 as the exciting source is shown in *Figure 8*. One coat of a typical paint, containing 30 per cent of titanium dioxide in the dried film, is about 0·001 inches thick. This corresponds to three milligrams per square centimetre on the graph, and is therefore well within the range of sensitive measurement.

Aluminium Coatings—Aluminium and other light elements are difficult to excite in this kind of apparatus. *Figure 9* shows how the thickness of aluminium on iron can be measured by recording the attenuation of the easily excited iron x-ray in the covering material. This approach could be used for other kinds of covering which are difficult to excite, *e.g.*, films of plastics, or paints without a convenient pigmenting element.

Analysis—Although the sensitivity of this apparatus is orders of ten below that of the conventional spectrometer it may still prove of value for specific applications. *Figure 10a* shows the response of the instrument, being used for simple solid analysis, to a catalyst used in petroleum refining; *Figure 10b* shows two traces superimposed from two samples, one of pure alumina and one of alumina containing one per cent tin and one per cent molybdenum.

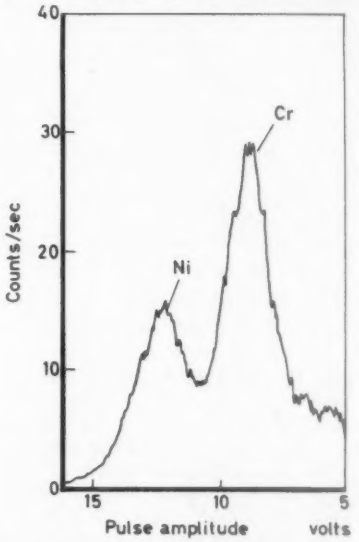

Figure 6. Chromium and nickel x-ray peaks from chromium plate

Future Developments of the Method

The results reported here are based on the use of comparatively small radioactive sources whose intensity could easily be increased by a factor of

ten or more if high count rates were desired, for better statistical accuracy or for shorter counting times.

This is important if the method is to be used for continuous non-destructive measurement in proces-

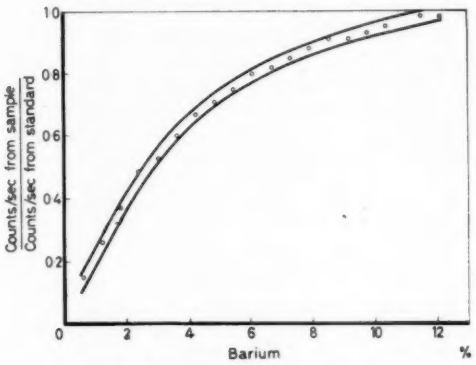

Figure 7. Measurement of barium solution strength with tungsten 181

ses which require short measuring times, for example in tin plate manufacture, as mentioned above. Pilot schemes using x-ray fluorescence with x-ray tube sources are being run both in the United States and in Britain at the present time for tin plate measurement. The apparatus involved is comparatively cumbrous, particularly for factory conditions, involving in one case a crystal monochromator, and in both cases either elaborate devices for stabilizing the x-ray tube output or else compensating devices to allow for variations in this output. It is hoped to avoid these difficulties by the use of the much simpler system using radioactive sources.

Choice of Suitable Sources

A number of radioactive isotopes can be used to provide sources for x-ray fluorescence work; the final choice of isotope will depend on the application, as the best results are obtained when the energy of the radiation from the source is the minimum that will excite the x-rays of the elements being investigated. The most important feature of the sources that can be used is that none of them emit any x-ray photons of more than about 80 keV in energy. Above this energy 'Compton scattering' becomes important in the interaction of x-rays with matter, and this scattering results in a continuous spectrum of degraded x-rays entering the counter and impairing the quality of the spectra.

Sources emitting beta particles, *i.e.* high speed electrons, can be used to produce fluorescent x-rays, but when these particles interact with matter the so-called Bremsstrahlung, or slowing-down radiation is also produced. This radiation has an energy spectrum extending from zero to the maximum energy of the beta particles emitted by the source. If a sample is bombarded with beta particles, therefore, this radiation will enter the counter and cause loss of sensitivity.

If a beta particle source is made, in which all the particles are absorbed as soon as they are emitted, then it becomes a pure Bremsstrahlung source, just as in an x-ray tube the absorption of electrons gives a continuous x-ray spectrum. If none of these

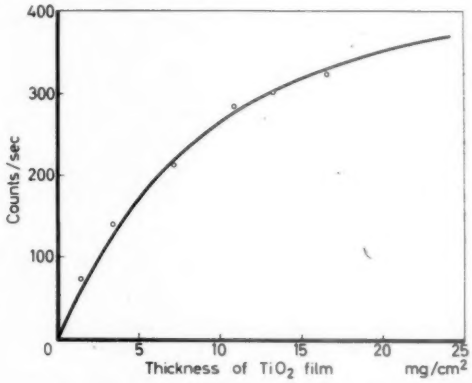

Figure 8. Measurement or titanium dioxide film thickness with caesium 131

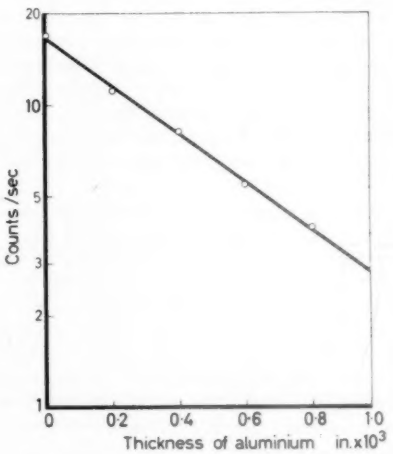

Figure 9. Measurement of aluminium film thickness with tungsten 181

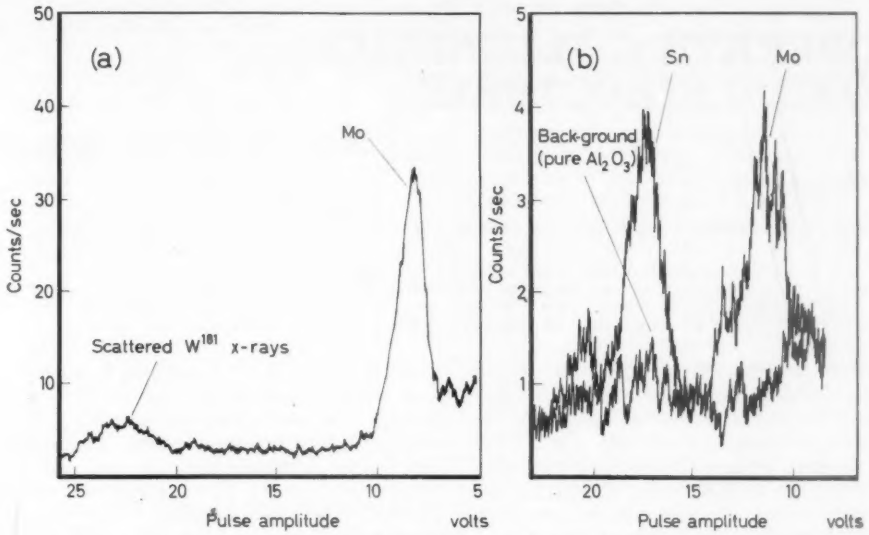

Figure 10. Apparatus used for solid analysis—(a) analysis of a catalyst used in petroleum refining and (b) two superimposed traces, one of pure alumina and the second of alumina containing one per cent each of tin and molybdenum

Bremsstrahlung are above about 60 keV in energy then the source can be used for this method of spectroscopy. The tritium source used for the measurement of chromium plate was in fact such a source; the maximum energy of the beta particles, which do not escape, is 16 keV, and so this is also the maximum energy of the Bremsstrahlung spectrum. The x-ray spectrum of such an exciting source is in fact very similar to the radiation from an x-ray tube running at 16 kV.

Alpha particles produce fluorescent x-rays without Bremsstrahlung, but unfortunately are about a thousand times less efficient than x-ray emitting sources, and so are not really a practicable proposition. The sources of iron 55, caesium 131, and tungsten 181 are ideal in that they only emit effectively monochromatic x-rays; the energies of these are 5·9, 29·6 and 56·9 keV respectively. The Compton effect does occur with radiation of these energies, but only to a very slight extent; some scattered x-rays from a tungsten 181 source are shown in *Figure 10*. Fluorescent excitation is most efficient if the energies of the exciting and excited radiation are close together. Thus tungsten 181 is the best of the trio for energies from 25 keV upwards, caesium 131 for energies in the range 5 keV to 25 keV, and iron 55 for energies of less than 5 keV.

Another source specially suited for this work is an isotope of the transuranic element americium, americium 241. This emits alpha particles, a 60 keV nuclear x-ray, and some x-rays of lower energy. In practice the alpha particles do not penetrate the source holder. At high energies its performance is like that of tungsten 181, but it is more efficient than the tungsten source at low energies because of the multiplicity of its x-ray emission. Its half-life, a very important consideration for sources that are to be used routinely, is 470 years, so that replacement is not a problem. This long half-life is an advantage that this source possesses over all the others mentioned here, whose half-lives are given below.

Americium 241	470 years
Caesium 131	9·7 days
Iron 55	2·9 years
Tritium	12·3 years
Tungsten 181	140 days

Of these sources, caesium 131 has too short a half-life ever to be used widely in this simple kind of x-ray spectrometer. All the others, however, are sufficiently long-lived to be of value. It can be confidently predicted that this method of spectroscopy, now in its infancy, will become widely used in the future to solve an increasing number and an increasing variety of scientific and industrial problems.

COOPERATIVE MAGNETISM IN OXIDE STRUCTURES

Part II—Ferrimagnetism

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The ferrimagnetic properties of certain oxides which crystallize in the spinel, magnetoplumbite, garnet and other structures are discussed in terms of indirect magnetic exchange interactions. The first part of this article, antiferromagnetism and ferromagnetism, was published in the May issue of RESEARCH.

THE WAY in which the indirect exchange of electron energy between magnetic cations leads to antiferromagnetism or ferromagnetism in certain oxide structures was discussed in the first part[1]. The general principle established that the exchange interaction occurs via excited states of intermediate anions, applies also to the third type of cooperative magnetism to be discussed in the present article.

In the now famous paper of 1948 L. NÉEL[2] extended the Weiss molecular field theory to a lattice containing two different magnetic sublattices. Negative exchange between ions on the different sublattice sites leads to antiparallel orientation of the sublattice moments, and, since these are of different magnitude, to a net magnetic moment. Néel proposed the term *ferrimagnetism* to convey the fact that ferromagnetic properties arise from what is essentially non-compensated antiferromagnetism*.

The non-equivalence of the sublattice moments may arise quite generally; either the different sublattices may correspond to different crystallographic sites or they may be crystallographically identical but occupied by different magnetic ions. When Néel first proposed the theory of ferrimagnetism only the former type of non-equivalence was known, but in the past few years examples of the latter type have been observed. The first such example[3] being pyrrhotite Fe_7S_8 in which the coordination of all iron ions is octahedral.

Space does not permit a discussion of the Néel theory but its far reaching influence on the whole field of non-metallic ferromagnetic materials will become apparent in what follows. The possible technical application of certain of the compounds was appreciated many years before their properties were understood. Their main advantage over the more conventional ferromagnetic metals and alloys is that they combine ferromagnetic properties with poor electrical conductivity (up to 10^{-12} that of metals). This means that the materials should be useful as magnetic core elements on account of their low eddy current loss. Also certain of the compounds form the basis of microwave gyrator elements of very low dielectric loss. The combination of properties is also useful to the theoretical physicist in so far that the low electronic conductivity precludes the influence of conduction electrons on the magnetic state of the system. Non-integral Bohr magneton numbers do not arise therefore as they do in the case of ferromagnetic metals.

*A brief description of the fundamentals of cooperative magnetism is given in Part I.

Spinel Structure—Ferrites

The term *ferrite* was originally given to that class of compounds obtained by reacting Fe_2O_3 with other metal oxides at high temperature, which crystallize in the cubic structure of the mineral spinel, $MgO.Al_2O_3$ or $MgAl_2O_4$. Nowadays the term is often used generically to denote magnetic oxides of any structure which contain iron. The most common form of a spinel-ferrite is $MeFe_2O_4$ where Me is a divalent metal such as Ni, Mg, Zn, Co *etc*—the mineral magnetite, Fe_3O_4 is ferrous ferrite $Fe^{2+}Fe_2O_4$—but other formulae exist for Me ions of different valency, *e.g.*, $Li_{0.5}Fe_{2.5}O_4$. In addition to the single ferrites, mixed crystal ferrites also occur. These may be formed by the partial substitution of other trivalent cations such as Cr, Mn, Al *etc* for the Fe^{3+} ions, or of other divalent ions for the basic divalent ion. The mixed ferrites are technically very much more important than the single ferrites.

In the spinel structure the metallic ions occupy two crystallographically different types of site: the tetrahedral *A* sites surrounded by four oxygen ions, and the octahedral *B* sites surrounded by six oxygen ions. The unit cell consists of eight formula units, *i.e.*, $Me_{24}O_{32}$ and has eight *A* and sixteen *B* sites occupied. This structure may be thought as arising from

the rock-salt structure ($Me_{32}O_{32}$) by removal of eight metal ions followed by slight displacement of a further eight ions from positions of octahedral to positions of tetrahedral coordination. The two basic octants of the unit cell are shown in *Figure 1*.

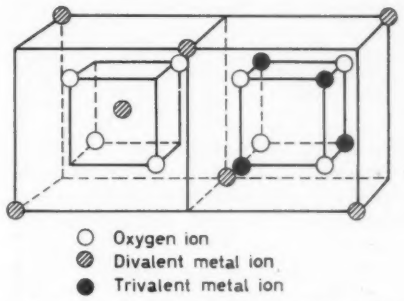

Figure 1. Two octants of the normal *spinel structure*

Ionic positions are different in octants that share a face and identical in those that share an edge.

The distribution of cations in the ferrospinel $MeFe_2O_4$ define three general types of structure:

(*i*) *Normal*, in which the *A* sites are occupied by Me ions and the *B* sites by the Fe ions, *e.g.*, zinc ferrite, which may be represented $Zn[Fe_2]O_4$.

(*ii*) *Inverse*, in which the Me ions are on *B* sites and the Fe ions equally divided among *A* and *B* sites, *e.g.*, nickel ferrite, $Fe[NiFe]O_4$.

(*iii*) *Intermediate*, in which the distribution of cations is intermediate between the extremes of the normal and inverse arrangements. An example of this type is magnesium ferrite, which may be represented $Fe_{1-x}Mg_x[Fe_{1+x}Mg_{1-x}]O_4$.

Factors which influence the distribution of cations among the two sites include the Coulomb (attractive) energy, the Born repulsive energy, the size and polarizability of the cations, and any individual preference of the ions for four or six fold coordination that results from their electronic configuration. Apart from the latter factor, which is very strong in some cases, for example Zn and Cd are mostly found on *A* sites due to their tendency to sp^3 bonding and Cr and Ni are attracted to the *B* sites due to crystalline field effects, the Coulomb energy probably contributes most to the lattice energy. This energy involves the charge distribution, the unit cell dimensions and the oxygen parameter (function of size of ions in *A* and *B* sites), but its final influence is greatly dependent on the polarizability of the cation in question. In addition to these factors, high temperatures tend to randomize the distribution and so produce the intermediate structure.

Ferrimagnetism

The spinel structure contains no linear configurations Me–O–Me but as stated in Part I this does not prevent the occurrence of strong superexchange interaction. The relative complexity of the structure provides many configurations of different angle and inter-ion distance. Of these by far the most favourable for superexchange interaction is a particular Me_A–O–Me_B configuration, and therefore the negative *AB* interaction is predominant in most ferrospinels. Next in order of strength is the negative *BB* interaction, while the *AA* interaction is the weakest. Since the occupation of the *A* and *B* sites by magnetic ions is different the antiparallel orientation of the sublattice moments leads to noncompensated antiferromagnetism, of ferrimagnetism. It is interesting that Néel had postulated that the magnetic character of ferrites arose through the antiparallel attraction of magnetic ions on octahedral sites and adjacent ions on tetrahedral sites, before the ideas of superexchange were fully worked out.

Assuming complete anti-parallel alignment of the sub-lattice moments, the molecular moment of a ferrite is given by

$$m = |m_B - m_A| \text{ in Bohr magnetons,}$$

where m_B and m_A are the sublattice moments. For

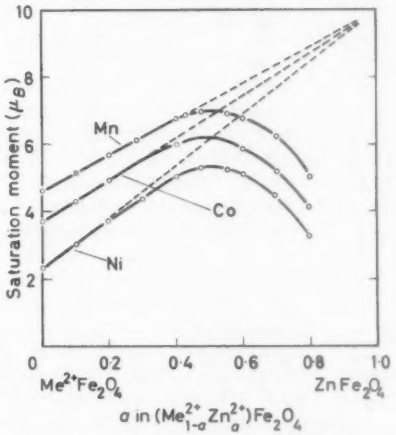

Figure 2. Saturation moment of mixed-crystal ferrites $Me^{2+}Fe_2O_4$. $ZnFe_2O_4$ (after Guilland et al[6,7])

the fully inverse arrangement $Fe^{3+}[Me^{2+}Fe^{3+}]O_4$ the moment is therefore

$$m = [(m_{Fe^{3+}} + m_{Me^{2+}}) - m_{Fe^{3+}}] = m_{Me^{2+}}.$$

If the orbital contribution to the atomic moments is neglected

$$m_{Me^{2+}} = 2S_{Me^{2+}}\mu_B$$

where *S* is the total spin quantum number. Thus, for

an ion with N unpaired $3d$ electrons (S equals $N/2$) the moment is $N\mu_B$. In this way Néel explained the fact that the molecular moment of Fe_3O_4 was about $4\mu_B$ whereas the molecule contained fourteen

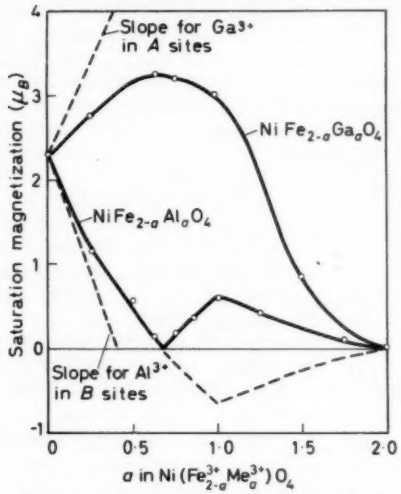

Figure 3. Saturation moment of mixed-crystal ferrites $NiFe_{2-a}Ga_aO_4$ and $NiFe_{2-a}Al_aO_4$ (annealed specimens; after Maxwell and Pickart[8])

unpaired electrons. Other inverse ferrites have molecular moments in close agreement with the $2S$ values. The slight departure found for example in nickel ferrite, where m is $2{\cdot}3\mu_B$ for a $2S$ value of two, is mainly due to the slight contribution of orbital momentum, which makes m equal gS where the g-factor is greater than two.

The molecular moment for the intermediate structure $Fe_{1-x}Me_x[Fe_{1+x}Me_{1-x}]O_4$, assuming spin only moments, is

$$m = 5[(1+x)-(1-x)] + 2S_{Me}[(1-x)-x]$$
$$= 10x + 2(1-2x)S_{Me}.$$

In the case of magnesium ferrite S_{Mg} is zero so that the molecular moment is a linear function of the magnesium ion distribution over the A and B sites. The distribution parameter x varies with the preparation (quench) temperature over the range about 0·09 to 0·26 and accordingly the molecular moment varies[4] from about 0·9 to $2{\cdot}6\mu_B$.

Only zinc and cadmium ferrites exhibit the completely normal structure (although not under all conditions) and they are also non-magnetic. In these compounds the magnetic Fe^{3+} ions occur wholly on the B sites, *e.g.*, $Zn[FeFe]O_4$ so there can be no AB interaction. The absence of ferrimagnetism is attributed to the random paramagnetic disorder of the atomic moments on the B sites above about 10°K, and to antiferromagnetic order below that temperature (Néel temperature).

Mixed Ferrites

The above three types of structure are beautifully illustrated by the independent work of E. W. GORTER[5] and C. GUILLAUD *et al.*[6] who measured the saturation moments of the mixed crystal series between inverse ferrites and zinc ferrite. Consider the system $(Ni_{1-a}Zn_a)Fe_2O_4$ where a varies from zero to one. If it is assumed that Zn ions preferentially occupy the A sites, as in $ZnFe_2O_4$, and Ni ions preferentially the B sites, as in $NiFe_2O_4$, then the following arrangements represent the complete system:

$a = 0$ $\quad Fe[NiFe]O_4$
$0 < a < 1$ $\quad Fe_{1-a}Zn_a[Ni_{1-a}Fe_{1+a}]O_4$,
$a = 1$ $\quad Zn[Fe_2]O_4$.

As Zn replaces Ni in the lattice an equivalent of Fe moves from the A to the B sites to preserve the 1:2 cation ratio between sites.

The molecular moment of the system at 0°K, assuming a predominant AB interaction, is given according to a previously deduced equation by

$$m = 2{\cdot}3 + 7{\cdot}7a,$$

taking $m_{Fe^{3+}}$ to be 5 and $m_{Ni^{3+}}$ to be $2{\cdot}3\mu_B$. This equation predicts that with increasing values of

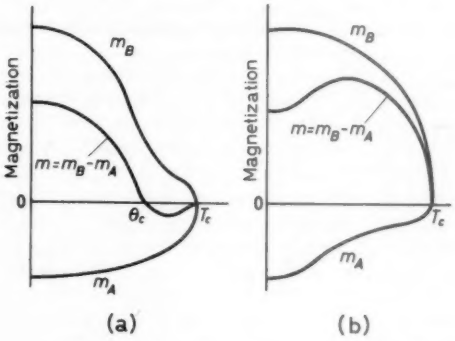

Figure 4. Schematic representation of anomalous magnetization versus temperature curves. The resultant magnetization (m) depends on the behaviour of the sublattice magnetizations (m_A and m_B). θ_c is the compensation temperature

a the molecular moment should increase from $2{\cdot}3\mu_B$ at $a = 0$ to $10\mu_B$ at a equals one. This cannot entirely be correct, however, as the composition a equals one is zinc ferrite which is non-magnetic. The reason for the anomaly is that with increasing values of a the basis of the above relationship

between m and a—that is, the negative AB interaction—is progressively destroyed as the number of magnetic ions on the A site is decreased. One might expect therefore that on substituting Zn for Ni in the system the saturation moment should initially increase according to the above equation but then gradually depart from it, ultimately becoming zero when a equals one. The results of Guillaud[6,7] for nickel, cobalt and manganese ferrite, which are illustrated in *Figure 2*, confirm this picture in a most striking manner.

Commercial use has been made of the relatively high magnetization of the mixed nickel–zinc and manganese–zinc ferrites, *e.g.*, the *Ferroxcubes*. Unfortunately these materials tend to have rather low Curie temperatures due to the weakened strength of the AB interaction. For example the Curie temperature of $MnFe_2O_4$ is about 300°C whereas that of $Mn_{0.6}Zn_{0.4}Fe_2O_4$ is near to 140°C.

The magnetization of ferrites is also lowered by substitution of other non-magnetic ions providing they preferentially enter the A sites. An interesting contrast in behaviour is observed, however, if ions that preferentially enter the B sites, such as Al^{3+} are substituted for Fe^{3+}. The effect of the substituted non-magnetic ion is to decrease the B sublattice moment until, in certain cases, it may become equal to the A sublattice moment when the overall magnetic moment becomes zero. Thus in the system $NiAl_aFe_{2-a}O_4$, zero moment is found for annealed specimens[5,8] at a equals 0·6. This value indicates that the Al^{3+} does not enter exclusively the B sites as in that case zero moment should occur at a equal to 0·46. With further substitution of Al^{3+} the moment increases due to the now dominant A sublattice moment (negative magnetization) finally falling to zero again for complete substitution ($NiAl_2O_4$). The data of L. R. MAXWELL and S. J. PICKART[8] for the substitution of Ga^{3+} and Al^{3+} in $NiFe_2O_4$ is graphed in *Figure 3*.

Influence of Temperature

A second way in which a zero magnetic moment can occur in certain otherwise 'ferrimagnetic' systems is through the anomalous temperature dependence of the B sublattice moment whereby at a critical temperature the two sublattice moments become equal. This situation is illustrated in *Figure 4a*. Below the critical or *compensation* temperature θ_c the moment of the B sublattice is greater than that of the A sublattice, while above this temperature the reverse is true. The direction of magnetization changes sign at the compensation temperature and this may be demonstrated directly. A rod of suitable material suspended in a weak horizontal magnetic field will rotate through 180° on being heated or cooled through the compensation temperature[9].

Ferrites which possess a compensation temperature are rare. The first system found to exhibit the phenomenon, which was predicted theoretically by Néel in 1948, was $Li_{0.5}Fe_{2.5-a}Cr_aO_4$ which results[5]

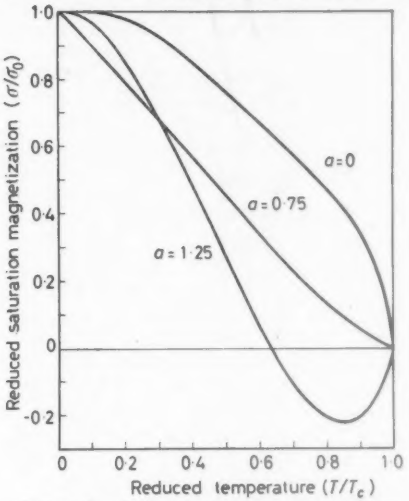

Figure 5. Reduced saturation magnetization versus temperature (σ/σ_0 versus T/T_c) curves for the mixed-crystal system $Li_{0.5}Fe_{2.5-a}Cr_aO_4$ (after Gorter[5])

from the substitution of Cr^{3+} for Fe^{3+} in lithium ferrite $Li_{0.5}Fe_{2.5}O_4$. With certain values of a, illustrated in *Figure 5*, the spontaneous magnetization decreases normally with temperature to zero, then increases, reaches a maximum, and finally falls again to zero at the Curie temperature.

The alternative possibility of the anomalous temperature dependence of the A sublattice moment was also discussed by Néel, who concluded that substances might exist whose spontaneous magnetization at first increased with temperature above 0°K and then decreased to zero at the Curie temperature, *c.f. Figure 4b*. Gorter[5] was the first to observe such behaviour in the system $Ni_{1.5-a}Mn_aFeTi_{0.5}O_4$, for compositions in the range $0{\cdot}4 < a < 0{\cdot}675$.

Hexagonal 'Ferrites'

A class of ferrimagnetic hexagonal iron oxide compounds, of which $BaO.6Fe_2O_3$ or $BaFe_{12}O_{19}$ is the prototype, was first described in 1952 by J. J. WENT and co-workers[10] from the Philips Research Laboratories, Eindhoven. The commercial interest in this type of material, which is marketed under the name *Ferroxdure*, lies in the fact that the easy

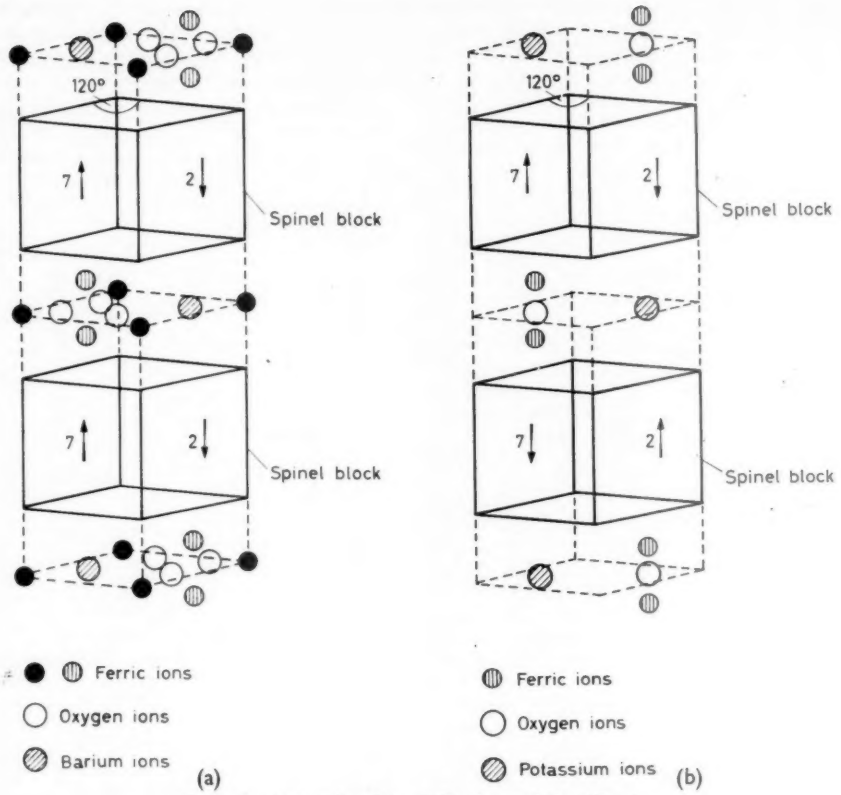

Figure 6. Unit cells of (*a*) $BaFe_{12}O_{19}$ *and* (*b*) $KFe_{11}O_{17}$

direction of magnetization is strongly coupled to the hexagonal axis. This results in a very large coercive force (up to 3000 oersted) so that the material, when suitably fabricated, can be used as a permanent magnet.

The crystal structure of $BaFe_{12}O_{19}$ was shown by V. ADELSKÖLD[11] in 1938 to be isomorphous with the mineral magnetoplumbite which has the approximate composition $Pb(Fe_{7\cdot5}Mn_{3\cdot5}Al_{0\cdot5}Ti_{0\cdot5})O_{19}$. The unit cell has dimensions $a = 5{\cdot}89$Å and $c = 23{\cdot}2$Å. The oxygen and barium ions together form a slightly expanded hexagonal close-packed lattice with the ferric ions occupying five non-equivalent interstitial sites. However, as indicated in *Figure 6a*, a large part of the structure is almost identical with that of the spinel lattice. In the layers between the spinel 'blocks' the oxygen lattice contains a Ba^{2+} ion, and in the same layer a Fe^{3+} ion is surrounded in an unusual way by a trigonal bipyramid of five oxygen ions. The remaining ferric ions occupy octahedral sites of different crystallographic positions and a tetrahedral site.

Within the spinel blocks there are nine Fe^{3+} ions of which seven have ionic moments pointing in one direction and two pointing in the opposite direction. By applying the Anderson rule of thumb method for superexchange interaction[1] it appears that in the complete unit cell the arrangement is sixteen $\uparrow Fe^{3+}$ and eight $Fe^{3+}\downarrow$. This gives a saturation moment at absolute zero of $40\mu_B$, in excellent agreement with observation. The room temperature saturation magnetization of barium ferrite is about 4600 gauss and the Curie temperature about 450°C.

The occurrence of non-compensated antiferromagnetism in the magnetoplumbite structure depends in detail on the structural composition between the spinel blocks. Thus, in the compound $K_2O.11Fe_2O_3$ or $KFe_{11}O_{17}$, which has a similar overall structure and almost identical unit cell dimensions to that of $BaFe_{12}O_{19}$, a difference in the

inter-block magnetic structure results in the occurrence of antiferro-magnetism. The spinel blocks are oriented antiparallel (*Figure 6b*) as a result of the interblock magnetic structure, and in the complete unit cell the arrangement is eleven $Fe^{3+}\uparrow$ and eleven $Fe^{3+}\downarrow$.

Ferroxplana

In the same 1952 paper[12] Went and co-workers also reported the analogous ferrimagnetic compound $BaO.2FeO.8Fe_2O_3$ or $BaFe_2^{2+}Fe_{16}^{3+}O_{27}$. The crystal structure differs from that of $BaFe_{12}O_{19}$ mainly in the composition of the 'spinel blocks' which contain now the equivalent of two formula units of Fe_3O_4. This raises the unit cell dimension to about 33Å in the *c*-direction.

More recently G. H. JONKER, H. P. J. WIJN and P. B. BRAUN[13] have extended the range of ferrimagnetic hexagonal compounds to ones containing iron, barium and a divalent metal of either the first transition group or of Mg or Zn. The crystal structures are related to the magnetoplumbite structure, having an almost identical *a*-axis unit cell dimension (about 5·9Å) but different *c*-axis dimensions. Three different general compositions exist:

Type *W*: $BaMe_2Fe_{16}O_{27}$ or $BaO.2MeO.8Fe_2O_3$ —*c*-dimension 32·8Å

Type *Y*: $Ba_2Me_2Fe_{12}O_{22}$ or $2BaO.2MeO.6Fe_2O_3$ —*c*-dimension 43·5Å

Type *Z*: $Ba_3Me_2Fe_{24}O_{41}$ or $3BaO.2MeO.12Fe_2O_3$ —*c*-dimension 52·2Å

where Me can be: Mn, Fe, Co, Ni, Zn or Mg.

An interesting and novel feature of the new compounds is that depending on the chemical composition the spontaneous magnetization lies either along the hexagonal axis, as in $BaFe_{12}O_{19}$, or perpendicular to this direction, *i.e.* in the basal plane. Compounds exhibiting the latter property are all those of type *Y* and those of types *W* and *Z* in which Co ions are completely or partially substituted for Me. Due to low crystal anisotropy the direction of magnetization can 'rotate' freely in the basal plane with the technically interesting result that these compounds respond to much higher frequencies (about 1000 Mc/s) before the onset of ferromagnetic resonance than is the case for the cubic ferrospinels (about 100 Mc/s). The generic name *Ferroxplana* has been given to the 'basal plane' compounds by Philips, Eindhoven, distinguishing them from their other products *Ferroxcube* and *Ferroxdure*.

Using the Anderson rule for the dependence of superexchange interaction on angle and inter-ionic distances in the various configurations Me–O–Me, and from low temperature saturation magnetization data, Gorter has predicted the magnetic structure of most of the type *X*, *Y* and *Z* compounds[14].

Rare Earth–Iron Garnets

Following earlier reports of interesting magnetic combinations of rare earths with ferric oxide, F. BERTAUT and F. FORRAT made a systematic study of the system M_2O_3–Fe_2O_3, where M is a rare earth metal ion, which resulted in the announcement[15] in 1956 of a new class of cubic ferrimagnetic compounds of formula $3M_2O_3.5Fe_2O_3$ or $M_3Fe_5O_{12}$. These compounds are isomorphous with the garnets of typical composition $Ca_3Fe_2(SiO_4)_3$, and may be considered as the result of the iso-electric double substitution

$$Ca^{2+},Si^{4+} \longrightarrow M^{3+},Fe^{3+}.$$

In each formula unit, which can be conveniently written $M_3Fe_2(FeO_4)_3$, there are three M^{3+} ions in 24 (*c*) sites of the unit cell having eight oxygen neighbours, two Fe^{3+} ions in 16 (*a*) octahedral sites and three Fe^{3+} ions in 24 (*d*) tetrahedral sites. The figures preceding the site letters are the total number of sites of each type in the structure.

The ferrimagnetic nature of the compounds was investigated by R. PAUTHENET[16] by measurement of the saturation magnetization down to 2·2°K, and by Bertaut and others in the case of yttrium-iron garnet $Y_3Fe_5O_{12}$ using neutron diffraction[17]. The results are consistent with the presence of three magnetic sublattices. Two unsymmetrical sublattices *A* and *D* are composed of Fe^{3+} ions in *a* and *d* sites respectively, and the third *C* sublattice is composed of the M^{3+} ions in *c* sites. The *A* and *D* sublattices, under the influence of strong negative exchange interactions, form a ferrimagnetic assembly after the manner of the ferrospinels. The resultant moment of the assembly is antiparallel to that of the *C* sublattice as a result of a further negative *CD* interaction.

If the rare earth ion is non-magnetic there is no *C* sublattice moment so that the saturation moment is merely the difference of two $Fe^{3+}\downarrow$ and three $Fe^{3+}\uparrow$, that is $5\mu_B$ for a single Fe^{3+} ion. The observed value of $Y_3Fe_5O_{12}$ is very close to this. In general, however, the saturation moment is given by

$$m_s = |3m_c - (3m_d - 2m_a)| = (3m_c - 5)\mu_B$$

The value of m_c, the moment of the M^{3+} ion, depends on the relative contribution of spin and orbital momenta. The absolute saturation moment of a rare earth ion, having quantum numbers *S* and *L*, is equal to $L+2S$ according to Hund's rule, but in most garnets the orbital contribution is not complete, so that the saturation moments lie between the spin only value of $(6S-5)\mu_B$ and $(3L+6S-5)\mu_B$, as shown in *Figure 7*.

As in the case of the spinel-type ferrites, the variation with temperature of the saturation magnetization depends in detail on the corresponding behaviour of the individual sublattice magnetizations. Three different forms of the variation are illustrated in *Figure 8*. Yttrium garnet exhibits the characteristic form associated with most ferrites as a consequence of the presence of only two magnetic sublattices. In other compounds containing the rare earth ions Gd, Tb, Dy, Ho, Er and Tm, the saturation magnetization of the *C* sublattice decreases more rapidly with temperature than that of the *A* and *D* sublattices, and as a consequence the compounds exhibit a compensation temperature. A third form of temperature variation is exhibited by $YbFe_5O_{12}$ which is non-magnetic at 2·2°K but becomes magnetic with increase in temperature, behaving as other compounds above their compensation temperature. The variation with temperature of the spontaneous magnetization of the ferric ions on each site can be calculated by the molecular field method of Néel for two sublattices. That of the M ions on the *c* sites is then obtained from the difference between the total magnetization of the compound and that calculated for the ferric ions.

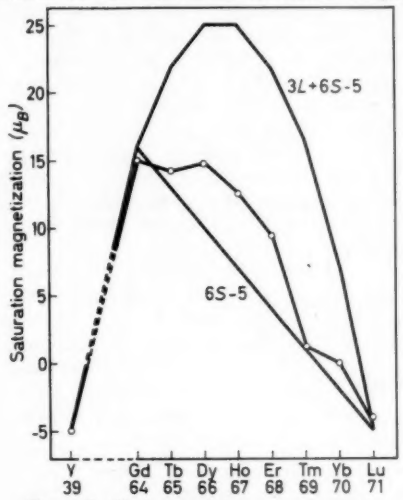

Figure 7. Variation of saturation magnetization per molecule with atomic number for the rare earth garnets $M_3Fe_5O_{12}$ (after Pauthenet[16])

The Curie temperatures of all the rare earth garnets lie in the close range 558±10°C, which suggests that the negative *AD* interaction is of greater strength than the negative *CD* interaction. In this respect it is most interesting that the shortest distance between the Fe^{3+} ions in the *a* and *d* sites are in almost perfect agreement with the ferrimagnetic distances found in spinel-type ferrites.

Substituted Garnets

There have appeared recently reports of the substitution of various metal ions for both the iron and rare earth components of ferrimagnetic garnets. Thus in yttrium and gadolinium garnets Al, Ga, Sc, In and Cr have been substituted for iron[18]. The change in properties of the compounds can be interpreted in terms of Al^{3+} and Ga^{3+} preferentially occupying the tetrahedral *d* sites, while the larger Sc^{3+} and In^{3+} ions preferentially occupy the larger octahedral *a* sites. Although the Cr^{3+} ion is small it enters the octahedral site, presumably on account of crystalline field effects (*c.f.* the spinel ferrites).

In accordance with the general composition of the *a* and *d* sites, octahedral substitution causes an initial decrease and tetrahedral substitution causes an initial increase in the magnetization. In all cases, due to a decrease in the number of Fe–O–Fe interactions, substitution of non-magnetic ions for Fe^{3+} leads to a decrease in the Curie temperature.

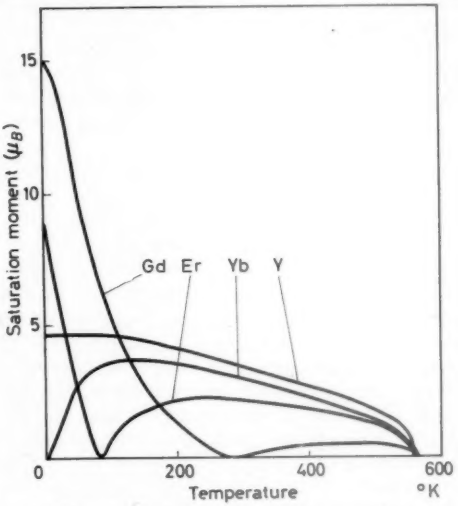

Figure 8. Variation of saturation magnetization with temperature for the rare earth garnets $M_3Fe_5O_{12}$ where M is Gd, Ev, Yb and Y (after Pauthenet[16])

Ferrimagnetism has recently been reported[19] in certain mixed crystals formed from the rare earth garnets and the iso-structural germanates, of general composition $X_3^{2+}Y_2^{3+}Ge_3^{4+}O_{12}$. The substituted garnet systems, *e.g.*, $(M_{3-a}^{3+}Mn_a^{2+})(Fe^{3+})_2(Fe_{3-a}^{3+}Ge_a^{4+})O_{12}$, represent a partial reversion to the form of the natural

silicate garnets through the partial isoelectric double substitution $M^{3+},Fe^{3+} \longrightarrow X^{2+},Ge^{4+}$.

Other Ferrimagnetic Structures

Finally we come to the situation in which ferrimagnetism occurs in compounds whose structure contain only one type of cation site. The non-compensated magnetic sublattices arise from an ordering of the magnetic species within the one type of crystallographic cation site. Such systems add to the already considerable generality of the Néel theory of ferrimagnetism.

The origin of antiferromagnetism in hematite, α-Fe_2O_3 and ilmenite, $FeTiO_3$ was explained in Part I as resulting from a negative exchange coupling between Fe^{3+} ions, or between Fe^{2+} and Ti^{4+} ions, on crystallographically identical sublattices. If the distribution of cation moments is altered in an ordered manner then uncompensated antiferromagnetism, *i.e.*, ferrimagnetism, should occur. Such ferrimagnetic properties have been found in the solid solution series $(1-a)FeTiO_3.aFe_2O_3$, or $Fe^{2+}_{1-a}Ti^{4+}_{1-a}Fe^{3+}_{2a}O_3$, for a equal to 0·45, and the explanation of the effect has been given in terms of cation ordering[20,21].

Another ferrimagnetic ilmenite-type compound where both magnetic sublattices have octahedral coordination is the recently described[22] compound $MnNiO_3$. The sublattices containing Mn^{4+} and Ni^{2+} are coupled antiparallel, and the measured saturation magnetization of $0{\cdot}76\mu_B$ is very close to the expected value for $Mn^{4+}\uparrow$ and $Ni^{2+}\downarrow$. Bertaut and Forrat[22] point out that in this compound the distance of the order of 3·5Å for the strongly interacting configuration Nn–Mi is the same as that found for the strong interaction configurations in ferrimagnetic spinels and garnets, and that this is perhaps highly significant to the theory of ferrimagnetism.

The final ferrimagnetic system to be mentioned is $Li_aNi_{1-a}O$, which J. B. Goodenough, D. G. Wickham and W. J. Croft[23] find to have a maximum saturation magnetization of 31cgs/cm^3/g at a equal to 0·46 and a maximum Curie temperature of 241°K at a equal to 0·41. Ferrimagnetism occurs over the range $0{\cdot}3 < a < 0{\cdot}5$. The lattice in this region is rhombohedral and all cation sites are equivalent. Ferrimagnetism is attributed to the partial ordering of Li and Ni ions into alternate sets of (111) planes which couple antiparallel to one another; it is postulated that the origin of the ordering forces being elastic rather than electrostatic in character.

Conclusion

Following the development of spinel-type ferrites the field of ferrimagnetism has expanded enormously to include widely diverse crystal systems. The main impetus behind the search for new ferrimagnetics has been the possible technical application of the materials, but, at the same time, much has been added to our knowledge of the mechanism of magnetic exchange interactions.

Sufficient advance has been made to establish the fact that non-compensated antiferromagnetism may be expected in a very large variety of oxide structures by suitable substitutions in the lattice.

It has not been possible to include in these articles details of the present day applications of ferrites and other ferrimagnetic compounds, but much of this information, together with the fundamentals of the subject, may be obtained from the reports of conferences held in recent years in America and London[24–28]. An excellent review of the radio and microwave frequency application of ferrites has been given by Gorter[29].

Figures 2, 7 and 8 are reproduced by courtesy of the Editor of Comptes Rendus, *Figure 3 by courtesy of the Editor of* Physical Reviews *and Figure 5 by courtesy of the Editor of* Philips Research Reports.

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THE USE OF RADIOACTIVE ISOTOPES

Part III—Inorganic Isotopes in Agriculture and Biology

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The first two parts*, by C. G. CLAYTON, dealt with the application of radioisotopes in engineering and metallurgy; the present article considers how radioisotopes are used in soil, plant and vertebrate studies.

RADIOISOTOPES are extraordinarily convenient tools for research in the field of inorganic biochemistry. Perhaps the main reason is the ease with which small quantities can be detected. For example, as one curie of pure potassium 42 weight $1{\cdot}6 \times 10^{-7}$ g and it is no very difficult task to detect 10^{-12} curies of most beta emitters, it is theoretically possible to follow $1{\cdot}6 \times 10^{-19}$ g of potassium, which could hardly be traced by any other technique.

So many papers have been written on this general field in the last few years that it is scarcely possible to mention their titles, let alone their contents, in a brief review of this kind. I propose to limit the discussion to isotope studies on soils, plants and vertebrates at the tracer level, and to omit the broad fields of radio entomology and the biological effects of radiation from consideration. Specific topics such as methods of handling tracers and analysis by radioactivation, which have been adequately reviewed elsewhere, are also omitted. Some of the material overlaps a review in this journal[1], and the subject is also treated in detail in several recent books[2–4]. Instead of considering the applications of each individual isotope, this review is divided into three sections describing soil, plant and animal studies respectively.

Isotopes in Soil Studies

Isotope techniques have been extensively used in tracing individual elements in the soil. The mobility of ions and their exchange properties can be followed with both ease and precision, but much work still has to be done in order to correlate the ion exchange properties of soils with their chemical structure.

This subject has recently been reviewed by C. B. AMPHLETT[5], and he points out that the three common clay minerals kaolinite, illite and montimorillonite have very different base exchange properties, which can be related to their structures as determined by X-ray diffraction. These minerals consist of complex aluminosilicate layers which are more or less negatively charged and are held together by positive ions, normally potassium. The latter are exchangeable, but some potassium may also be more tightly bound within the layers and this is referred to as 'fixed' or non-exchangeable potassium. It has been shown[6] that the alkali metal cations K^+, Rb^+ and Cs^+ can become fixed on vermiculite, but smaller divalent and trivalent cations are much less strongly fixed. This accounts for the anomalous behaviour of the alkali metals in certain soil studies. Experiments with fission products have established that the order of ion mobility in soils is: Rb^+, Sr^{2+}, Y^{3+}, Zr^{4+}, and Cs^+, Ba^{2+}, La^{3+} and Pu^{4+}. We might expect the rates of ion uptake by plants will follow the same series, but in fact the uptake of rubidium and caesium is generally much lower than that of strontium and barium, presumably because of the soil fixation phenomenon; no such anomaly is found when plants take up the same elements from water culture.

Soil fixation has also been effectively demonstrated for phosphates labelled with P^{32}. It is particularly marked in latosolic soils of tropical regions, but is not confined to them, as it has been noted in Britain in the basalt soils of Antrim and the liassic soils of Leicestershire. Tracer studies have confirmed that phosphorus fixation is more complex than potassium fixation, since the phosphate can be fixed in at least three distinct ways: on acid soils it may be fixed as insoluble iron and aluminium phosphates; on soils rich in humus it may be adsorbed on to the organic fraction to give insoluble, and therefore probably polymeric, organic phosphates; and it can be very strongly absorbed by many clay minerals, where it probably enters the lattice structure. Thus the total phosphorus in a soil bears little relation to the amount available to plants, though the latter can be estimated by isotopic dilution[7].

Isotopic dilution has also been used to determine available sulphur, calcium, iron, cobalt and zinc in soils[8–12]. (*Figure 1* gives values for the different rates

*Part I was published in April (page 148) and Part II in May (page 172)

of leaching of calcium and chloride ions in sandy soil.) Iron is of particular interest in that despite its abundance and wide distribution it is often fixed as an insoluble oxide in alkaline soils, giving rise to chlorosis in the endemic vegetation. Salts labelled with Fe^{59} have been used[13,14] to show that certain chelating agents, notably ethylenediaminetetraacetic acid and *trans*-1,2-diaminocyclohexanetetraacetic

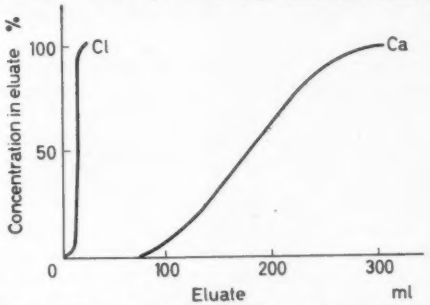

Figure 1. Different rates of leaching calcium and chloride ions in sandy soil—from Orcutt, *et al., Oak Ridge, T.I.D. 7517 (1955)*

acid are capable of supplying iron in a soluble form even in alkaline soils. Fixation of manganese added to the soil as $Mn^{54}SO_4$ has been demonstrated[15].

The release of nutrients to soils during the process of mineral weathering has apparently not yet been studied by isotopic techniques but it should be possible to activate representative minerals with neutrons for several months and then study their breakdown by natural agencies like frost, percolating water, plant roots, and soil microorganisms. Elements whose release could be studied in this way include phosphorus, sulphur, calcium, iron, cobalt, zinc, rubidium, strontium and caesium which all have isotopes of long half life. Fundamental research of this kind has perhaps been neglected because of the many applied problems which have urgently demanded solution. For example, there are very many published papers on experiments with labelled fertilizers[16], and these have yielded information on the best time to apply fertilizers and where to place them for individual soils and crops. (*Figure 2* shows plants being tested to determine the amount of phosphorus taken up from isotopically labelled fertilizers.) Other applications include studies of fertilizer mixing, of leakages in irrigation dams used for rice growing, and of the extent and direction of drainage in pineapple plantations. Labelled soil could also be used to compare the efficiency of different methods of washing roots, but no such studies have been published.

Isotopes in Plant Studies

Our knowledge of the uptake, distribution and function of metals in plants has been greatly extended by the use of radioactive tracers. For example, E. EPSTEIN and his collaborators[17–19] have made substantial contributions to our understanding of the kinetics and mechanism of the uptake of ions from nutrient solutions. They have used the hypothesis that the metabolic transfer of ions, which takes place against a big osmotic gradient, involves a system of carriers which can assist the ions across cell membranes. Although univalent cations do not compete with divalent cations for the same carrier, potassium, rubidium and caesium compete with one another but do not interfere with sodium uptake. In the same way calcium, strontium and barium compete for an unknown carrier, but magnesium uses a different carrier.

Recent work has shown that more than one carrier is involved for these cations[20], as it is for the uptake of phosphate[21], and it would be very interesting to determine the nature of the carrier for potassium, since this element forms very few covalent compounds apart from a complex with salicylaldehyde. J. L. GAMBLE[22] has used K^{42} in one attempt to find out how this element is bound in tissue, and other workers[23] have shown that phosphate is needed to form the carrier for manganese.

The uptake of ions from soils is much less well understood than it is from nutrient solutions. One difficulty which is not present in solution work is the problem of equilibrating added labelled atoms with their stable isotopes present in the soil. Under natural conditions it may take several years for added fertilizer to equilibrate with the soil, if indeed the soil can ever be said to be in equilibrium at all. Most investigators have not troubled about this problem and have labelled soil by thoroughly mixing in a solution of a carrier-free radioisotope. Using this technique, for example, it has been shown[24] that the amounts of rubidium and caesium absorbed by plants from many different soils depend on the amount of available potassium present: in the same way the amounts of strontium and barium taken up were shown to depend on the available calcium. I. V. GULIAKIN and E. V. YUDINTSEVA[25] have made extensive investigations of the behaviour of long-lived fission products in plants and soils, and the results are of general interest. Strontium is taken up much more freely than all other fission products: although caesium has a higher mobility, it is more strongly bound by most soils. The findings of K. H. LARSON and collaborators, who have shown how different soil conditions can modify the absorption of fission products, have recently been summarized[26].

The growing interest in fall-out has stimulated research into the foliar absorption of plant nutrients. More than half the radioactive fall-out in plants is absorbed directly through the leaves, and a recent review[27] shows how efficient foliar absorption can be. Radioisotopes have been used extensively in this work, which has shown that not merely leaves, but stems and even the bark of full grown trees are permeable to applied solutions, especially under humid conditions. Some nutrients can also be leached from leaves by artificial rain. It is unlikely that the fertilization of the soil will ever be supplanted by the spraying of liquid nutrients, but some deficiency conditions can be treated more easily by sprays than by any other means. Leaf absorption of sulphur dioxide, for example, may provide all the sulphur necessary for plant growth in areas of industrial pollution.

The translocation and storage of radioisotopes in plants can be followed either by direct counting of suitably shielded portions of the plant[28] or by autoradiography of freeze-dried specimens[29,30]. Many interesting qualitative observations have been made

Figure 2. Testing of leaves with Geiger counters for phosphorus uptake at the Rothampstead Experimental Station. Fertilizer labelled with phosphorus 32 was mixed with the soil before the plants were sown. (Crown Copyright Reserved)

by the latter technique, for example the striking concentration of zinc in the seeds of the tomato[31], and the precipitation of iron phosphate inside the xylem which can lead to iron deficiency[32], but few elements have yet had their distribution exhaustively studied at different stages of growth.

The rate and mechanism of flow of several elements has been unequivocally demonstrated using isotopes[33]. Potassium and phosphate travel upwards through the xylem and downwards through the phloem. (*Figure 3* shows the injection of apple trees with a solution containing phosphorus 32.) Elements like calcium, iron and zinc will move upwards but not downwards in plants, so if they are applied as foliar sprays they cannot correct deficiencies in the roots.

The study of the function of major and minor elements in plants is as yet in its infancy, and radioisotopes should find increasing use here. Tracer work has showed[34,35] that considerable amounts of zinc and of cobalt are closely associated with the protein fraction of leaf extracts. The power of radioisotope studies is well illustrated by work[36] on the enzyme nitrate reductase. This confirmed that this enzyme contained molybdenum as an essential constituent by showing that the enzyme activity was proportional to Mo^{99} content during the various stages of purification, and the whole subject has recently been summarized in a masterly review article[37].

Radioisotopes can also be used to trace the depth of penetration of roots[38], the compatibility of stock and scion[39], and to study the distribution of fungal spores[40]. Such studies do not require specific radioisotopes.

Isotopes in Vertebrate Studies

Isotopes have probably been more widely used in vertebrate studies than in any other single field. There are relatively few elements which cannot be labelled without increasing the normal amount of the element in the body. However, tracer studies have shown that for most elements the amount metabolized depends critically on the chemical form in which they are administered. For example, cobalt retention is much better when labelled vitamin B_{12} is fed to an animal than when inorganic cobalt spiked with Co^{60} is used[41]. This means that care must be taken in labelling foodstuffs if valid results are to be obtained. Vegetable foods can often be labelled by growing them in soil or solutions containing the required tracer, and animal foods could be labelled in the same way.

In particular, percentages of different elements that are metabolized, the half-life in the body, and the mode of excretion are easily studied by tracer methods. High urinary excretion of tracer which has been fed orally[42–44], as is found for sodium, potassium, and sulphur, indicates efficient absorption through the walls of the intestine and a high rate of metabolic turnover. When excretion of the

Figure 3. Experiments using phosphorus 32 to induce mutations in trees and shrubs for ultimately improving the crop, e.g., *Cox's Orange Pippin, gooseberry without prickles*, etc. *This was the first method used for the injection of radioactive phosphorus* (*Crown Copyright Reserved*)

tracer is largely faecal, as it is for calcium, the heavy metals and most of the minor essential elements[45–47], it does not necessarily mean that the element is not extensively metabolized. Inorganic ions can cross the gut wall in either direction, and calcium has been shown to do this[48–49] in some ingenious labelling experiments. These experiments showed that although 95 per cent of labelled calcium was excreted in the faeces, more than 25 per cent was initially absorbed through the gut wall, all but five per cent crossing the gut wall again to appear in the faeces. In the same way it was shown[50], using P^{32}, that lambs can digest 95 per cent of the phosphorus in lucerne, though the apparent digestibility in a conventional balance experiment was only 31 per cent. The apparent digestibility is a meaningless figure, and only the tracer method can give a true picture of intestinal metabolism.

Tracers are also used for following the rates at which ions circulate in the bloodstream and for studying numerous other rate processes in animal physiology. Intravenous injection of a radioisotope is used when absorption from the intestine is very low, and it has been used for practically every element in the periodic table. A characteristic feature is the rapid equilibration of the isotope in the blood; the specific activity of the blood becomes constant in a matter of minutes[51]. Equally characteristic is the rapid removal of elements foreign to

the bloodstream. Thus manganese, which is present only in minute traces in blood[52], is rapidly removed after intravenous injection in rats, only 0·08 per cent remaining in the blood after five hours[53]. Certain

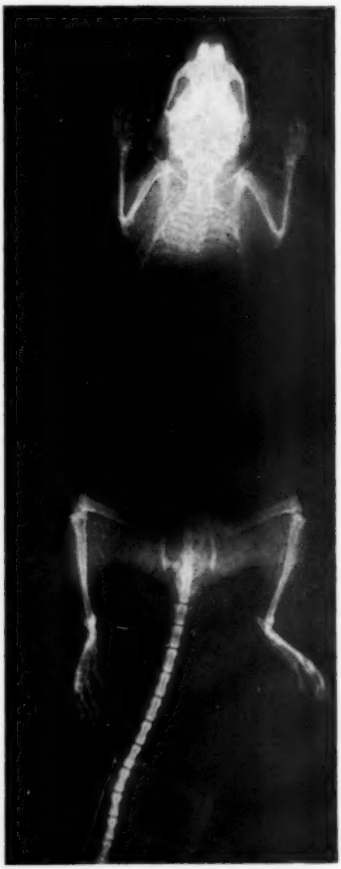

Figure 4. Autoradiograph of a mouse which has received an intraperitoneal injection of yttrium 90—from Strahlen therapie Sonderband (1958) **38**, 348

isotopes, such as S^{35}, K^{42}, Cr^{51}, Fe^{59}, and Se^{75} are selectively absorbed by red blood cells, and some of these have been used for determining the number[54] and average life of red blood corpuscles[55]. Isotope dilution techniques using radioactive sodium have also been used to determine the volume of extracellular fluid in the body[56].

The distribution of radioisotopes after administration to animals can be followed to a limited extent by external counting. Quantitative figures for the distribution of individual elements are best obtained by dissecting, ashing and counting the different tissues or aliquots of them. The qualitative distribution can be followed by autoradiography, and for weak beta emitters like Ca^{45} this technique can give quite good resolution of microscopic detail. (An autoradiograph of a mouse which has received an intraperitoneal injection of radioactive yttrium is shown in *Figure 4*.) The study of inorganic metabolism in embryos and research on bone growth[57] have greatly profited from autoradiographic techniques. Thus E. E. SMITH and P. GRAY[58] have investigated the distribution of Cu^{64} in the developing chick embryo, and D. D. DZIEWIATKOWSKI[59] has shown how sulphur concentrates in the cartilage tissue of embryo rats. Copper is known to accumulate in the livers of young animals[46], but the reason for this is unknown. Tracer studies also indicate that copper accumulates in the liver and spleen of cancerous mice[60]. The distribution and metabolism of poisonous elements like beryllium, arsenic and antimony have been examined using tracers[61–63] and the monumental studies of J. G. HAMILTON[64] on the metabolism of the fission products of uranium and plutonium deserve mention.

The study of trace element function in vertebrates has only just begun, and we can expect important advances in the next decade. In many instances simple cytological facts are lacking, as I know of no comprehensive study of the distribution of radioisotopes of essential trace elements in different cellular fractions, though the stable isotopes have been investigated[65]. It has been shown[66] that copper is much more abundant in the cytoplasm of liver cells than in the nuclei, though it is present in both. L. S. MAYNARD and G. C. COTZIAS[53] have confirmed earlier observations[67] of the same finding for manganese, and have further shown that this element is preferentially absorbed on the mitochondria, an important site for enzyme activity. It was also found that zinc concentrates in egg yolk[68] where it appears to be strongly bound to lipovitellin, and recently a remarkable cadmium protein has been isolated[69]. Molybdenum has been proved to be an essential constituent of xanthine oxidase from milk[70] by isotopic dilution with Mo^{99}; studies[71–73,41] with I^{131} in thyroxine, Fe^{59} in cytochrome C and ferritin, and Co^{60} in vitamin B_{12} have shown the power of tracer techniques.

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LIVING POLYMERS

Their Preparation and Application

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New processes of polymerization are described, in which the initiation and termination reactions are controlled. Under these conditions the molecular weight and the sharp molecular weight distribution of the polymer are controllable. The use of these polymers and block copolymers is proposed for a systematic investigation of the physical properties important in practical applications.

IN RECENT years, striking advances have been made in the development and use of man-made materials derived from high polymers, that is to say, long chain molecules formed by the linking together of simple monomer units. In the application of such substances, knowledge of the factors which determine the mechanical and physical properties of the polymers is essential and, although a certain amount of such information is available, there is a need for more systematic approach to these problems than has previously been made. In this paper are described recent developments which, it is suggested, can be utilized for such an approach. It is also suggested that this method may prove to be of direct large scale preparative value for polymers of improved properties.

Mechanisms of Polymerization

The polymers we are concerned with here are addition polymers derived from vinyl monomers of the type $CH_2{=}CH.X$, where X can be one of a number of chemical groups or atoms. These monomers can be polymerized by virtue of the reactive double bond[1], which can be opened up, forming a reactive species to which another molecule of monomer can be added. In this way long chains of the type

$$CH_2CHX \cdot\cdot\cdot\cdot CH_2CHX \cdot\cdot\cdot\cdot CH_2CHX$$

can be formed.

There are three purely chemical ways in which this double bond can react leading to polymerization: by reaction with a free radical species (*I*), or by reaction with a generalized (' Lewis ') acid (*II*) or base (*III*):

$$R\cdot + CH_2{=}CHX \longrightarrow R.CH_2{-}\dot{C}HX \quad \ldots\ (I)$$

$$A^+ + CH_2{=}CHX \longrightarrow A.CH_2{-}\overset{+}{C}HX \quad \ldots\ (II)$$

(from acid)

$$B^- + CH_2{=}CHX \longrightarrow B.CH_2{-}\bar{C}HX \quad \ldots\ (III)$$

(from base)

In case (*II*), reactive 'carbonium' ions are formed and in case (*III*) 'carbanions' are formed, but in all cases the polymer molecule grows by a chain process subsequent to one of the *initiating* reactions. In the *propagation* reactions, successive molecules of monomer add to the reactive entities and form increasingly larger units, the growth of which is ultimately stopped by some *termination* reaction 'killing' the growing polymer. The stages of such a mechanism are shown below for the anionic polymerization of styrene by potassamide in liquid ammonia[2].

Initiation

$$NH_2^- + CH_2{=}CHPh \longrightarrow NH_2.CH_2{-}\bar{C}HPh \quad \ldots\ (IV)$$

Propagation

$$NH_2.CH_2{-}\bar{C}HPh + CH_2{=}CHPh \longrightarrow NH_2.CH_2CHPh.CH_2.\bar{C}HPh \quad \ldots\ (V)$$

$$NH_2.CH_2[CHPh.CH_2]_n\bar{C}HPh + CH_2{=}CHPh \longrightarrow NH_2.CH_2[CHPh.CH_2]_{n+1} + \bar{C}HPh \quad \ldots\ (VI)$$

Termination by Proton Transfer from Solvent

$$\text{----}\bar{C}HPh + NH_3 \longrightarrow \text{----}CH_2Ph + NH_2^- \quad \ldots\ (VII)$$

Termination by Chain Transfer to Monomer

$$\text{----}\bar{C}HPh + CH_2{=}CHPh \longrightarrow \text{----}CH_2Ph + \bar{C}H_2.CHPh \quad \ldots\ (VIII)$$

In this case the initiating reaction is of type (*III*) above, and the growing polymer is therefore a carbanion. The termination reaction is the relatively facile one of proton transfer from the solvent, so few molecules attain a great size before undergoing this reaction. As a result, only polymers of low molecular weight (1000 to 6000) are obtained in this process[2].

Other reactions are, in general, possible, but the only one which need be mentioned here is that of chain transfer (*VIII*), in which the original growing polymer is killed and growth of a new polymer chain continued from another molecule of monomer.

The interplay of these various steps in the polymerization process determines the characteristics of the overall reaction, as well as the properties, in particular the distribution of molecular weights, of the resulting polymer.

Molecular Weight Distribution

Since not all the polymer molecules will grow to the same extent before undergoing termination, different molecules will contain different numbers of monomer units. This means that the molecular weight of a polymer sample is not a definite number, identical for each molecule, as in such substances as potassium chloride or strychnine. Instead, there will be a distribution of molecular weights which may be quite broad, the various molecules present ranging in molecular weight from a few thousands up to more than a million.

This is best illustrated by means of a molecular weight distribution curve, in which the fraction by weight of each component of the whole polymer is plotted against the molecular weight (*Figure 1*). The distribution is characterized by various average molecular weights which may be measured. Most important are the number average $\bar{M}_n$ and the weight average $\bar{M}_w$ molecular weights. The ratio of these quantities is a measure of the breadth of the distribution: if $\bar{M}_w/\bar{M}_n$ is about 1 to 1·5, then the polymer has a narrow distribution, but some commercial materials may have $\bar{M}_w/\bar{M}_n$ of about ten, and cover a wide range of molecular weights.

Many of the mechanical and physical properties of importance in the applications of polymers are profoundly influenced by this distribution of molecular weights, although in some cases other factors may be of equal importance (*cf. Figure 2*). For example, in low pressure polythenes, certain properties depend almost entirely on the degree of crystallinity, whilst others are determined by both the crystallinity and the molecular weight[3]. *Table 1* shows how, in the case of a vinyl chloride–vinyl acetate copolymer, various technologically important properties are influenced by the molecular weight[4].

Clearly, there is a marked decrease of all these properties with molecular weight, and, for example, a certain molecular weight is necessary for any mechanical strength to be developed at all. This means that the presence of low molecular weight constituents will considerably reduce the strength and utility of the polymer, and prevent the attainment of the best possible properties of the material. On the other hand, if the molecular weight is too high, the viscosity of the molten polymer may become so high that moulding of the material

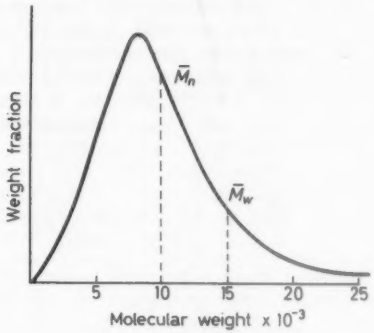


Figure 1. Typical molecular weight distribution curve $\bar{M}_n$ *is 10,000 and* $\bar{M}_w/\bar{M}_n$ *is 1·5*

becomes difficult. There is therefore an optimum range of molecular weights for particular uses of a given polymer. In the case of polystyrene, all the physical properties reach a limiting value at a particular molecular weight[5]. It thus becomes possible to state, for example, that to obtain a film of polystyrene of maximum tensile strength, the distribution must be such that $\bar{M}_n$ must be greater than 20,000 and $\bar{M}_w$ greater than 130,000, simultaneously.

Now such results as these were obtained by fractionation of the original polymer into a number of fractions of sharper molecular weight distribution. This is a particularly difficult process to carry out on the large scale necessary to yield sufficient quantity of material for physical testing, and it may still not give polymer of very sharp distribution. As a result, not a lot of this type of information seems to be available, though it is obviously essential if the greatest use of the polymers is to be made. A valuable new approach to these problems would be provided by a method of direct preparation of polymers having a very narrow molecular weight distribution. Some recent work may well provide such a method.

Formation of 'Living' Polymers

By considering some aspects of the mechanism of anionic polymerization, such as that shown in (*IV*) to (*VIII*) M. SZWARC has shown how a novel

preparative method might arise and, with his collaborators, has realized this in practice[8–11]. This process, involving the formation of what Szwarc has called 'living' polymers, is novel in two respects. The first of these relates to the termination reaction. It was previously mentioned that a relatively rapid termination step leads to the formation of low molecular weight polymer, and that it is responsible for the distribution of molecular weights. However, if this termination step does not occur, then the polymer will continue to grow until all the available monomer has been consumed, but it will then remain 'live' indefinitely. The living, reactive ends may then be killed when desired, *after* the polymerization has been completed. This allows, in principle, a much greater control of the molecular weight of the polymer than is possible when termination is occurring throughout its growth.

How, then, can this termination process be controlled? In the case of anionic polymerization, transfer of a proton from the solvent, as in reaction (*VII*), must be prevented. This can be achieved by working in a non-proton donating solvent. At the same time, it is necessary to prevent the carbanions giving up their electrons to any other species present, and this requires the use of a solvent which solvates the carbanions well. Both of these conditions are satisfied by tetrahydrofurane, and Szwarc has shown that in this solvent, 'living' polymers can be formed.

In this solvent he has also used a novel initiating reaction, utilizing the green complex formed between sodium and naphthalene. The intensely coloured [Na^+, naphthalene$^-$] initiates polymerization by transfer of an electron from the naphthalene anion to, say, styrene monomer. This is a reaction similar to (*III*), but *only* an electron is transferred, so that no foreign group is introduced into the monomer. A radical-ion, $\dot{C}H_2$–$\bar{C}$HPh, is formed, which could grow simultaneously by both a radical and an anionic mechanism; but according to Szwarc, these species dimerize at low temperatures to form carbanions which then grow by successive reactions with monomer until it is all consumed. The reaction as shown below, terminates on the addition of water.

Initiation

$$Na^+C_{10}H_8^- + CH_2{=}CHPh \longrightarrow$$

$$CH_2{=}\bar{C}HPh + Na^+ + C_{10}H_8 \qquad \ldots . (IX)$$

$$\downarrow$$

$$\cdot CH_2{-}CH{:}$$
$$\quad\ Ph$$

Propagation

$$2\ {:}CHPh{-}CH_2\cdot \longrightarrow {:}CH{-}CH_2CH_2{-}CH{:} \qquad \ldots . (X)$$
$$\qquad\qquad\qquad\quad Ph \qquad\qquad Ph$$

$$2\ CH_2{=}CHPh + {:}CH{-}CH_2{-}CH_2{-}CH{:} \longrightarrow$$
$$\qquad\qquad\qquad\quad Ph \qquad\qquad Ph$$

$${:}CH{-}CH_2{-}CH{-}CH_2{-}CH_2{-}CH{-}CH_2{-}CH \quad (XI)$$
$$\quad Ph \qquad Ph \qquad\qquad Ph \qquad Ph$$

Termination upon the Addition of Water

$${:}CH\text{----}CH{:} + 2H_2O \longrightarrow CH_2\text{----}CH_2 + 2OH^- \quad (XII)$$
$$\quad Ph \qquad Ph \qquad\qquad\qquad Ph \qquad Ph$$

In the case of polystyrene, the 'living' ends consists of the group

$$\text{----}CH{:}$$
$$\qquad Ph$$

so the living polymer has the bright red colour of the negative benzyl ion, and the formation of living polymer results in the instantaneous formation of this colour in place of the green colour of the catalyst. Since the electron affinity of the benzyl radical is much higher there is no transfer of an

Table 1. Effect of molecular weight on physical properties of polymers

Material	*Molecular weight*	*Tensile strength* (lb/sq.in.)	*Impact strength*	*Modulus of elasticity* (lb/sq.in.)	*Modulus of rupture*
Whole polymer	10,600	9025	0·25	400,000	13,300
A	15,800	9955	0.36	418,000	14,400
C	13,200	9630	0·32	401,000	13,000
E	7500	6680	0·16	394,000	9100
F	5800	1120	—	350,000	1470

electron from the living polymer back to the naphthalene, which would be seen as a change of colour from red back to green.

The red colour is, however, immediately destroyed upon the addition of a drop of water, since the living

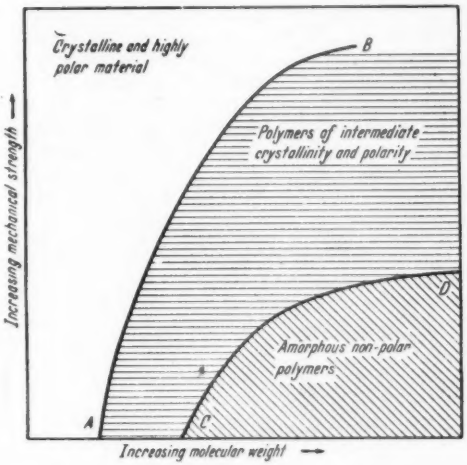


Figure 2. Dependence of mechanical properties of high polymers on molecular weight—reproduced from a paper by H. Mark in Industrial and Engineering Chemistry *(Copyright American Chemical Society, 1942)*

ends react immediately and are killed. A similar loss of colour occurs in the presence of oxygen, but in this case there is also a considerable increase in the molecular weight of the polymer. It is supposed that the oxygen removed an electron from the living ends, yielding radicals which subsequently undergo dimerization,

$$\text{----}\underset{\text{Ph}}{\text{CH}}\text{:} + O_2 \longrightarrow \text{----}\underset{\text{Ph}}{\text{CH}}\cdot + O_2^- \quad \ldots\ldots (XIII)$$

Using this technique, a number of polymers have been prepared; in all cases the living polymer was finally killed with water (see *Table 2*). An important feature of the process is that high conversion of monomer to polymer occurs, and yields of up to 96 per cent have been reported. A further important consequence is that the molecular weight is controllable, and is given by the expression

$$\text{Molecular weight} = 2M_0 \frac{\text{(Moles of monomer)}}{\text{(Moles of catalyst)}} \quad \ldots\ldots (XIV)$$

where M_0 is the moleuclar weight of the monomer. The molecular weight of the polymer is therefore independent of the concentration of monomer or catalyst, and of the temperature of the reaction. Furthermore, the molecular weight distribution is extremely narrow; provided certain conditions are satisfied, it is the so-called Poisson distribution.

When growth of the polymer proceeds under conditions which afford equal opportunities for all the molecules, and in the absence of transfer reactions, then a remarkably narrow distribution of molecular weights is formed. It can be shown that if ν is the number of molecules of monomer per polymer molecule, then

$$\overline{M}_w/\overline{M}_n = 1 + \nu/(1 + \nu)^2 \quad \ldots\ldots (XV)$$

Therefore, the relative breadth of the molecular weight distribution decreases with the increase of the extent of polymerization. The distribution is much narrower than any obtainable by fractionation, and according to P. J. FLORY, 'it is doubtful if the degree of heterogeneity associated with a Poisson distribution as a high degree of polymerization could be distinguished from absolute homogeneity by any known physical method'[12].

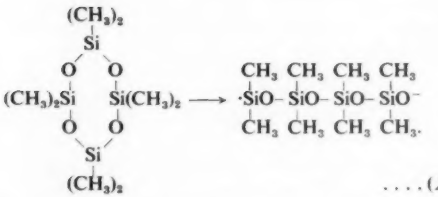
Applications of 'Living' Polymers

This technique of anionic polymerization without termination would appear, then, to provide a method for the preparation of vinyl polymers with controllable and very narrow molecular weight distribution. This is borne out by the reported values for $\overline{M}_w/\overline{M}_n$ of 1·06 to 1·12 for polystyrene made in this way. Use of this method should provide, therefore, materials in suitable quantities for a systematic study of physical and mechanical properties. It would make possible direct measurements of these properties as a function of molecular weight, without resort to the tedium of fractionation. Further, by a blending of the virtually homogeneous polymers, the preparation of material of desired properties should be made considerably easier. Laboratory investigations of this type might well reveal how materials of enhanced valuable properties could be produced. Large scale production of polymers by this method may then prove desirable, possibly as a source of polymers for subsequent blending.

Recently an extension of this technique to the polymerization of the important silicon compounds has been reported[13]. It has been shown that potassium naphthalene will catalyze the polymerization of octamethylcyclotetrasiloxane in tetrahydrofuran solution, with a yield of about 70 per cent. Electron transfer to the cyclic monomer $[(CH_3)_2SiO]_4$ leads to ring opening following by formation of a silanolate radical ion as shown in (*XVI*).

Table 2

Monomer	*Temperature* (°C)	*Molecular weight*	*References*
Styrene, CH_2=CHPh	−78 to 0	12,000–190,000	8
Butadiene, CH_2=CH.CH=CH_2	−78	22,000–63,000	10
Isoprene, CH_2=CMe.CH=CH_2	0	25,000–400,000	10
Methyl methacrylate, CH_2=CMe.COOMe	−78	—	9



. . . . (*XVI*)

It appears that subsequent reaction results in the incorporation of a catalyst residue—substituted dihydronaphthalene ion—at one end of each polymer chain. Polymers have been derived from cyclic, ethylene oxides in a similar way.

A further application of the technique arises in the preparation of *block copolymers*. Copolymers are formed when two monomers, A, B, are polymerized together, yielding a product such as

. . . . AAABBABAABBBA . . . .

In the search for new and superior materials, attention has turned recently to the preparation of block copolymers, in which the monomeric units are not distributed at random, but are in definite groups or blocks,

. . . . AAAABBBBBBBAAAA . . . .

Up to the present, activity has been largely confined to the development of laboratory methods of preparation, and the use of ' living ' polymers provides a further method.

If monomer A is added to the living polymer derived from monomer B, then owing to the propagation reactions of the type (*XI*), the further living polymer will be of the block type. This can then be killed directly, or further monomer(s) added on to the structure. Clearly, there are many variations in the structure of the block copolymers which could be prepared,

. . . . BBBBAAAABBBBAAAABBBB . . . .

and . . . . CCCAAAABBBBAAAACCC . . . .

Production of block copolymers from styrene and methyl methacrylate has been reported[9], but several important aspects of this application remain to be investigated. These include the susceptibilities of different monomers to block copolymerization on to living polymers, and the control of molecular weight, and its distribution, in the product. However, it constitutes a promising method.

The limitations and difficulties of the general technique must be indicated. Firstly, there is the limitation as to monomer, which obviously must be susceptible to anionic polymerization. This is determined[14] by the nature of the substituent group X in the monomer CH_2=CHX, where X can be any one of the following

Radical

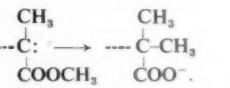
X = CN, CO_2Me, OAc, CH=CH_2, C_6H_4Cl, C_6H_5,

Anionic

CH_3, OAlk, C_6H_4OMe.

Cationic

In general, the wide range of monomers subject to radical polymerization would be subject to anionic polymerization, though several monomers remain to be investigated. With certain monomers which are susceptible, however, a further limitation may arise: for example, the living polymethyl methacrylate is self-killing[9], and the reactive ends are rapidly destroyed, possibly by some intermolecular reaction such as



. . . . (*XVI*)

Then there are the limitations of practical technique. Szwarc has stressed the need for scrupulous cleanliness if the quantitative aspects of the reaction, particularly equation (*XIV*), are to be realized.

Owing to the high reactivity of the living polymers, minute amounts of impurities in the monomer or solvent, or adsorbed on the walls of the reaction vessel, have a considerable effect on the reaction. Further, these difficulties are increased in the preparation of higher molecular weight polymers and this is reflected in the relatively low molecular

weights so far attained (see, for example, *Table 2*); whilst the presence of small amounts of water or oxygen will lead to reactions (*XII*) and (*XIII*) above, which will destroy or modify the living ends.

In the case of butadiene, impurities may completely prevent polymerization by this technique[10], but in general it will still occur, though yielding a much broader distribution of molecular weights. These practical difficulties can, with care, be overcome on the laboratory scale, but they present considerable problems in a large scale use of the procedure. On the other hand, they may prove to be no greater than those arising in the use of the recently developed, highly reactive, catalysts for polymerization processes.

The preparation of block copolymers is also beset with some limitations, probably the most serious of which is the occurrence of chain transfer reactions, such as (*VIII*), above. These lead to the formation of polymers derived from the monomers separately. For example, if methyl methacrylate is added to living polystyrene, some 55 per cent of block polymer is formed, but the methyl methacrylate acts as a chain transfer agent and polymethyl methacrylate and polystyrene are also formed[10]. This is undesirable and the separation of the resulting mixed polymers is a difficult and wasteful process, though it arises to some extent with most methods of preparation. Chain transfer reactions also have a serious effect in broadening the molecular weight distribution.

'Monodisperse' Polystyrene

Another method of polymerization in which the initiation and termination steps are controlled has recently been described[15]. So far this technique has only been applied to styrene, but it gives polymers of molecular weight in the range 500,000 to 2,500,000, that is, considerably greater than the Szwarc technique in yields of over 50 per cent. The method depends on *intermittent* initiation and termination, the growing chains being kept apart by using a water emulsion system, so that each chain grows in its own separate droplet or micells. Initiation occurs by photochemical means, by exposing the monomer to light of a sufficient energy ($\lambda\nu$) to open the double bond. The growth of the polymer chain occurs between these intermittent exposures: at 0°C about two minute intervals are required for a molecular weight of one million to be reached. At present the use of such a technique is rather limited, and large scale is likely to be much more difficult than with the procedure described by Szwarc.

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1959 Essay Competition for Schools and Technical Colleges

Entries for this competition are now being accepted but please remember that individual entries will not be acknowledged. *The final closing date is July 31st, 1959.*

Section I: a report (about 800 words) on any piece of practical work or project in biology, chemistry or physics written by a school student whose *16th birthday falls on or after June 1st, 1959.*

Section II: a longer report (about 1000/1500 words) on a similar subject to section I, written by a school student *over the age of 16 on June 1st, 1959.*

Section III: a critical essay (about 1000/1500 words) on which of the 'new' metals promises to be most useful in technology. This section is open to any student attending a technical college who is *under the age of 21 on June 1st, 1959.*

RESEARCH

The 1959 Waverley Gold Medal Essay Competition

RESEARCH is this year sponsoring The Waverley Gold Medal Essay Competition for the seventh year in succession. The Competition is designed to encourage the scientist in the laboratory and the engineer in the production plant to express his views and translate his work into an essay that will readily be understood by other scientists, directors of industrial firms and others interested in science and technology.

The **Waverley Gold Medal**, named after and bearing the coat of arms of the late Lord Waverley, together with **£100** will be awarded for the best essay of about 3,000 words describing a new scientific project or practical development giving an outline of the scientific background, the experimental results and the potential application of the project or process in industry. The essays will be judged for technical content by specialists in the subject, for clarity of presentation and for style.

A second prize of **£50** will be awarded and also a special prize of **£50** for the best entry from a competitor under the age of thirty on 31st July 1959. If the first prize is awarded to a competitor under the age of thirty, the special prize will go to the next best entry. For full details write to the Editor of RESEARCH, 4/5 Bell Yard, London, W.C.2.

All entries must be received by the Editor not later than 31st July 1959

SURVEY

Royal Society Conversazione

Traditionally the Royal Society Conversazione is held each year in mid-May. It is open only to Fellows of the Society and their guests. As usual, the subjects were varied, ranging from viruses to x-ray fluorescent analysis* and the skidding of motor vehicles. Two of the topics are briefly reviewed here.

Was Lysenko Right?

Dr A. DURRANT of the Institute of Rural Science, Aberystwyth, has been conducting a series of experiments with one species of flax derived from a stock in commercial use in Northern Ireland and he has found that changes which were transmitted from parent to offspring could be induced purely by different environmental conditions. The first generation of plants were treated with two different combinations of inorganic fertilizers, *i.e.*, different ratios of nitrogen, potassium and phosphorus and these treatments resulted in two distinct types of plant. The first was a light plant with short side branches and the second was much heavier, perhaps three or four times as heavy, with long side branches. Five successive generations have been bred from these plants, without further fertilizer treatment, and the changes appear to be permanent. Cross-breeding experiments have produced hybrids that are intermediate in size between both kinds of parent. This would be expected only if the genetic constitution of the two plants had been changed by the initial fertilizer treatment.

These results are in complete contradiction to current views on genetics and Dr Durrant is, of course, very anxious that further experiments should be carried out to confirm the results. This question of environment being able to affect the inherited characteristics of any species permanently was part of the cause of the Lysenko controversy, when Lysenko claimed to have adapted winter wheat to Arctic conditions. (Lysenko also claimed that the chromosomes played no part in the inheritance of characteristics.) The work at Aberystwyth seems to show that environments can affect the chromosomes and, if confirmed, these results will undoubtedly change some of the current concepts of inheritance.

Impact of Liquids at High Velocities

Dr F. P. BOWDEN of Cambridge University and some of his colleagues showed the effect that the impact of liquid, in this case water at velocities of up to 3000 miles per hour, can have on a stationary solid surface. The result of such impacts appears to be catastrophic on most materials: aluminium is deeply pitted and Perspex almost completely shattered. This work relates to the very practical problem of high speed aircraft and missiles flying through rain. At about 500 miles per hour or more, the impact of raindrops results in rapid deterioration of leading edges and can cause the complete shattering of Perspex windscreens. It appears that the only thing to do if an aircraft flying at supersonic speed meets rain, is to dive out of it as quickly as possible!

* See the article by Dr MELLISH on page 212

Transistor Exhibition and Convention

An international exhibition and convention was recently held in London devoted to semiconducting devices and their associated circuitry. The transistor as such was first invented only eleven years ago by Professor J. BARDEEN, Dr W. H. BRATTAIN and Dr W. SHOCKLEY who were awarded the Nobel Prize for their work. These three American scientists presented the opening lectures at the convention. Dr Brattain, in a delightful and easy style of lecturing, traced the early history of semiconducting devices while Professor Bardeen reviewed the progress that had been made over the past decade in basic research on semiconductors. (The original type of transistor, a point-contact device, is now already obsolete.)

Dr Shockley spoke of the future. He thought that future developments would lead to solid circuitry and he and his colleagues were working on devices which he called 'transistor diodes'. Four-layer transistor diodes only require two wire connections instead of the three used by transistors and, Dr Shockley claimed, that circuits which previously required two or more transistors as well as other components can now use these minute devices. The four-layer transistor diode has been in commercial production for two years and its particular application so far has been in high speed digital computers where a time of one millionth of a second is taken to extract any one of 80,000 pieces of information from its magnetic memory store.

In the exhibition itself there were a variety of interesting displays. Many German and Japanese firms are in the transistor market but their display stands were rather bare with the emphasis on the sale of standard ranges of transistors and equipment and not on technical achievement or specialized products. The trend is, of course, to higher frequencies, greater power and smaller size. Texas Instruments were showing their miniature solid circuits produced in the United States (mentioned in last month's *Survey*) and very high frequency transistors, up to about 600 Mc/s. The British manufacturers are offering 100 Mc/s transistors in

their standard ranges and development models of 200 Mc/s. There was a notable absence of devices that resemble thermoionic tetrodes in behaviour and the General Electric Co. of America appears to have the only successful development model available at the moment. Solid state devices of materials other than germanium and silicon were also in evidence: Birmingham University showed some of their development work on cadmium sulphide diodes using an indium cathode.

More Semiconducting Devices

The short history of semiconducting devices is an exciting story of success, and recently Mullard invited the press to Southampton to show them the success of their two-year old plant.

It was interesting to note that both germanium high-frequency and power transistors* are now in full scale production. Problems do arise in the production of transistors for higher frequencies, for the dimensions of the components get progressively smaller as the frequencies are increased (see *Figure 1*) and in some cases all the assembly work must be carried out under binocular microscopes. The techniques used for preparing germanium single crystals of the required purity, cutting and etching the wafers, alloying the emitter and collector and assembling the transistors are now reasonably 'standard'. Mullard still use batch processes but it is expected that these will be replaced progressively by automatic systems within the next few years.

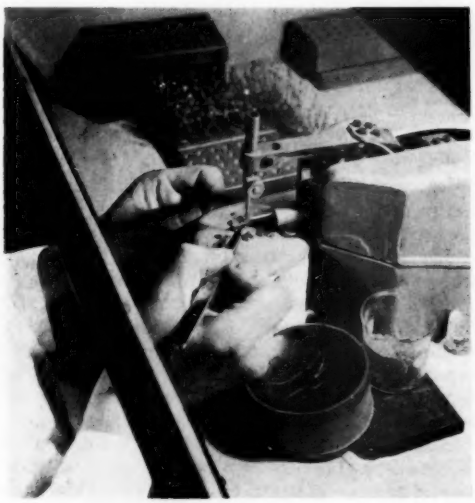

Figure 1. Mullard Semiconductor Plant, Southampton—an operator assembling an alloy transistor on to the glass base. This illustration gives some idea of the difficulties that can arise when working with minute components

Silicon transistors form a very small part of the total output at present but the demand for these devices, which will operate at higher ambient temperatures than germanium transistors, is steadily increasing. Unlike most other firms, Mullards have selected to make alloyed-junction silicon transistors† and there are only two other firms in the world who use this particular method because of the technical difficulties involved. Alloying will, however, produce cheaper transistors, as demanded by the civilian market, and the process is thought to be more suitable for large scale production.

Transistors are obviously big business. Twenty million semiconductor devices will be produced at Southampton this year and this means an annual turnover of about £20 million. Mullard's success must be attributed to the amount invested in research and development—a current figure of around £250,000 was quoted—and of course to the high proportion of graduate scientists and engineers employed on this plant, about seven per cent of the total pay-roll. Mullard were emphatic that transistors did not mean the death of conventional valves—although more limited ranges of valves would probably be produced with a consequent drop in price—but they do seem to have developed semiconducting devices whose market prices are considerably cheaper than those of their competitors and will therefore have general application even in inexpensive 'electronic' boxes. It is anticipated that the price of Mullard transistors will be reduced by something like 25 per cent in the very near future.

New Theory of the Expanding Universe

A new theory that would explain the expansion of the universe in terms of known forces has recently been developed by Dr R. A. LYTTLETON and Professor H. BONDI. Briefly, the theory rests on the hypothesis that the magnitude of the charge of the proton exceeds that of the electron by about two parts in 10^{18}. Such a difference would mean that the smoothed-out background material of the universe would have volume charge sufficient to produce an electrical repulsion giving the observed expansion rate. The galaxies and clusters of galaxies occur in the theory as condensations in ionized regions, and take part in the expansion

* See also the articles on high-frequency and power transistors—*Research, Lond.* (1958) **11**, 425; (1959) **12**, 21

† See *Research, Lond.* (1958) **11**, 381

because they form and continue to grow from the dispersing background material, which is maintained at constant density by continual creation of matter.

The theory has other consequences. For example, potential differences of the order of 10^{19} volts occur between ionized units (galaxies and clusters), and the charge-excess is driven off from them as protons with energy of this order—a value that corresponds in general order to the maximum energies attained by cosmic ray particles. In this way the theory may give a reasonable explanation of how these ultra-high energy cosmic rays are produced.

The charge-excess required by the theory could equally well result from a slight excess in the number of protons over electrons everywhere with their charges exactly equal and opposite. In either form of the hypothesis, creation of matter implies creation of charge, and the Maxwell equations accordingly require a minute amendment involving cosmical terms.

If the proton and electron charges do differ slightly, very small particles of matter would necessarily have non-vanishing electric charge. No experiments made to date would have disclosed the requisite small charge difference, but it is just possible that tests could be devised that would do so, and establish how closely the two charges do in fact approximate to equality in magnitude.

Water Pollution Research Laboratory

The Water Pollution Research Laboratory is concerned with all aspects of the pollution of surface waters and its control. The work of this laboratory —which is perhaps not as widely known as it should be—is concerned with the treatment of sewage and industrial wastes and the effect of pollution on natural waters.

Two items shown to visitors on May 6th were of particular current interest: trials with a new type of detergent, which has already been incorporated in *Tide*, and the effect of increased radioactivity on plant and fish life. The ' new ' detergent is an alkyl aryl sulphonate, similar to most of the detergents in current use except that it has a straight alkyl chain, and it has been found with pilot plant scale trials that as much as 94 per cent is destroyed by normal sewage treatment. This means that the amount of detergent in sewage effluent would be decreased from 4·2 p.p.m. to about 0·8 or 0·9 p.p.m. (Alkyl sulphonates such as *Dreft* do not cause foaming.)

The level of radiostrontium from fall-out is ' rather high at the moment ' and it appears that both soil and plants act as filters. This filtering effect of plants is not really desirable for when the plants die at the end of the season there may be a sudden release of concentrated amounts of strontium 90.

Figure 2. Water Pollution Research Laboratory, Stevenage—photographic survey of the River Ivel. The water here is about two feet deep. The camera is carried by the balloon and is operated by an electric trigger from the boat. A mosaic pattern of the vegetation of the river bed can be built up from these photographs

As would be expected, there is a wide difference in strontium uptake from hard and soft waters. The calcium ions in hard water reduce the probability that the strontium, with similar chemical properties, will be utilized by plants or fish. There is also a marked difference in the amounts absorbed by individual species: blanket weed, for example, may take up about ten to one hundred times more radiostrontium than a rooted plant like watercress.

The effect of plants on streams varies throughout the year. They control the amount of oxygen in the water, the pH value and the velocity of the water. A survey of the River Ivel has been carried out which shows that the yield of water weed during the summer of 1958 was about that of cultivated hay crops (1·44 g organic carbon/m²/day)! An aerial photographic method has been developed for studying the distri-

bution of the various species in rivers (see *Figure 2*); the method is limited to fairly shallow rivers less than 40 ft wide. The apparatus consists of a polythene balloon filled with hydrogen, below which is an automatic camera, stabilized by a gimbal and secured to a light-alloy frame. The shutter is operated electrically, thus enabling a whole series of photographs to be taken by sending pulses of electricity up a cable from a 12-volt battery on the ground. Mosaics may be built up of a stretch of river from component photographs and the distribution of different plant species can be mapped from such mosaics.

Mr R. W. EDWARDS also mentioned the problem of midge larvae and that a great deal of swarming had been encountered near Stevenage. It was not certain whether midges were capable of or did in fact carry diseases, but it was proposed to put this matter to the test in the very near future. It might be possible to find specific poisons that would settle on the river bed and would only be eaten by the larvae and not by the fish. It remained to be seen whether the fish would eat the dead, poisoned larvae.

Non-Ferrous Metals Research

The work of the British Non-Ferrous Metals Research Association is perhaps rather better known than that of the Water Pollution Research Laboratory. The Association has a wide range of published work to its credit, some of which is certainly of the highest quality. The two things which caught the eye of visitors at the opening of the extension to their laboratories was, firstly, the work on crack-free chromium and, secondly, the investigation of thorium alloys.

The problem of cracks in chromium plate is one that is continuously with the car industry and it seems as though no easy solution is at hand. Extensive work has shown that improvements can be obtained by increasing nickel thickness, increasing chromium thickness, excluding nitrogen (this was first discovered by Australian workers) and by altering the bath composition. It seems, however, that any practical solution will be a balance of these four variables and, as these depend on the shape of the article to be plated, it is probable that the solution will be empirical and each manufacturer will have to adjust the process according to the part to be plated. Crack-resistance can be realized by increasing both temperature and current density but in this case 'burnt' patches will be obtained at places of very high current density, *i.e.*, at the edges of articles. One thing is reasonably certain: by adjusting these variables a very much improved product can definitely be obtained.

The work on thorium is aimed at developing alloys suitable for use in nuclear reactors and, judging by the results seen here, it appears that a great deal more has to be done before a suitable thorium alloy can be developed for use in a nuclear reactor without a metallic sheath. Such an alloy would have to have considerable tensile strength in the region of 600° or even 800°C and would have to be sufficiently creep-resistant not to show serious distortion after nuclear bombardment for perhaps up to one or two years.

The most probable material is a thorium cermet but many oxide and carbide systems are reduced by thorium and the only possibility seems to be thorium–zirconium carbide or thorium–niobium carbide; the niobium carbide is very expensive, about £35 per kilogram. The zirconium carbide cermet has a sharp drop in tensile strength around 600°C, from ten tons per square inch to at least half this value. Creep tests are being carried out but the results were not yet available.

New Elastomers Laboratory

In 1960 Du Pont will open a new factory near Londonderry for the manufacture of general-purpose synthetic rubber. As a complement to this they have opened a research laboratory at Hemel Hempstead, at which the qualities of different synthetic rubber compounds can be tested. The new laboratory is equipped with apparatus designed to reproduce exactly the normal manufacturing processes and to test the properties of the products. There are three main sections of which the first deals with dry processing, as used in the production of solid rubber articles such as car tyres, wire insulation, *etc* and the second is devoted to fluid processing by which such products as rubber gloves, foam rubber mattresses, paints and coatings are fabricated. The demonstration at the official opening included the making of a rubber glove by dipping a form into rubber solution and then into a salt solution, whereupon the synthetic rubber solidified immediately and the glove could be peeled off the form.

The third, and probably the most interesting, section is the physical testing area. Here the most dramatic apparatus is a 'weatherometer' which can simulate a wide range of weather conditions: there are also ovens for artificial ageing, a cabinet for testing resistance to ozone, apparatus for testing electrical properties, abrasion and cracking resistance, *etc*. A 'universal testing machine' measures a very wide range of physical properties such as stress and strain characteristics, tear resistance, tensile strength and adhesion at temperatures ranging from −56° to about 300°C.

The synthetic rubbers which Du Pont are promoting in the United Kingdom are *Neoprene* (chloroprene polymers), *Hypalon* (chlorosulphonated polyethylene) and *Viton* (a copolymer of vinylide fluoride and hexafluorpropylene)*. *Neoprene* is the product which was used during the war and with post war improvements, it is claimed to be superior to natural rubber in certain applications such as for the treads of motor vehicle tyres. *Hypalon* is a more expensive product, but is very durable particularly in the form of coatings and paints. The flooring in the laboratory entrance hall in a very attractive blue colour with a beautiful glossy finish was made of *Hypalon*. The finish is apparently permanent and requires no polishing. This type of floor covering is in particular demand for commercial and industrial purposes but is at present rather expensive for domestic use; it retails at between 70*s* and 80*s* per square yard. *Viton* is remarkable in its resistance to high temperatures and to some of the ' exotic ' fuels. It can be used at temperatures up to 240°C in continuous service and at 320°C in intermittent service.

The laboratory has two aims—to develop improved finished products from synthetic rubbers and to provide technical assistance to Du Pont's customers, not only in the United Kingdom but throughout Europe, Africa, Australia and in parts of Asia. No original research is being carried out at present, but there is room for expansion and Du Pont evidently intends to expand both in the size of the premises and the range of work to be carried out.

Chapelcross Power Station

A new nuclear power station, a newer edition of Calder Hall, has started to operate at Chapelcross. This is the second British nuclear station and the fourth in the world. Chapelcross, when all its reactors are working at maximum capacity, will add 184 MW of electricity to the national grid but it would still be rather more honest if it were called a munitions factory, for that is what it is. When the station was first planned about two years ago, thoughts of even partial disarmament were very far away and it was designed to produce primarily plutonium and secondly electric power. Should the need for plutonium be lessened by the disarmament talks it will, of course, be possible to allow the fuel elements to remain in the reactor for longer periods. This will increase its efficiency as a power station but it will not compare with either coal-fired or the later nuclear stations. (At the moment it is intended that fuel rods should remain in the reactor for about 6 to 12 months.)

* See also *Research, Lond.* (1959) 12, 7

The design, with the exception of the layout of the two turbine halls, is almost identical to that of Calder Hall. The reactors use natural uranium, graphite moderated and cooled with carbon dioxide gas and each reactor contains over 10,000 fuel elements, nearly 130 tons of uranium. The reactors operate at temperatures of 400 to 410°C and must be shut down for reloading (see *Figure 3*).

Figure 3. Chapelcross Nuclear Power Station—a general view of the charge floor of No. 1 reactor showing the charge and discharge machines for loading and unloading fuel elements. The reactor must, of course, be shut down before this operation can take place

The only substantial alteration compared with Calder Hall is a device for measuring the Wigner energy which has been incorporated in the last three reactors but not in No. 1 reactor which is already operating. The device is a means of measuring the dimensions of the whole reactor core, first when the reactor is cold and secondly when the reactor first reaches a temperature of 400°C. At this stage practically no Wigner energy will have accumulated and therefore the difference between the dimensions of the reactor at 400°C initially and at 400°C at a later stage (when Wigner energy has been stored), is expected to give an adequate indication of the total Wigner energy. The only other means of measuring this energy is by withdrawing samples of the graphite which have been inside the reactor core and measuring their heat content.

BOOK REVIEWS

Introduction to Neutron Physics

L. F. CURTISS

(*391 pp; 9¼ in. by 6 in.*)
London: D. Van Nostrand. 73*s*

MANY readers who see the title of Dr CURTISS' book will think of nuclear reactors, which are much associated in the public mind with neutrons : indeed, the introduction on the jacket recommends the book to all who are likely to work with nuclear reactors. However, the great virtue of this book is that it puts *pile* neutron physics in its proper perspective as just a part of neutron physics. In fact only about a dozen pages are devoted to descriptions of reactors, as one of the available sources of neutrons, and apart from this the reactor physicist finds his place among other users of neutrons.

The scope of the book will be indicated by the main chapter headings such as particle and nuclear interactions, sources, detection, spectrometers and monochromators, interactions with matter, calibrations and standards, shielding and protection of personnel. The emphasis is on the experimental facts, and methods, and the book brings together in a balanced way much information which is only available in widely dispersed journals. Mathematic equations are quoted but any detailed derivations of these are relegated to an appendix, with the result that the main chapters offer a very readable account of the subject.

Of necessity some of the descriptions are highly condensed but a good list of references to original papers is provided at the end of each chapter. Each chapter also carries a collection of numerical problems, though it seems a pity that the solutions are not provided as an encouragement to the reader to tackle them. The book is very fully illustrated with 250 or so line drawings, including many original semi-diagrammatic sketches of experimental apparatus which are particularly attractive.

G. E. BACON

Nondestructive Testing

J. F. HINSLEY

(*xxxiv+495 pp; 9 in. by 6 in.*)
London: Macdonald & Evans. 75*s*

POTTERY and bell foundry are among the most ancient crafts which have always practised nondestructive testing of their ware. The wheel-tapper has been a familiar sight since the early days of rail transport. Then, in his epoch making publication in which Röntgen (whose initials were W. *C.* R.) '*gave* the whole discovery [of x-rays] to the world in January 1896', he also showed clearly the way to x-ray radiography. The medical world was at once ready and eager to make use of the new technique, whereas the beginnings with industrial radiography were only made twenty years later, under the stress of war and with the advent of the aeroplane. Since those early days gamma ray radiography, neutron radiography, magnetic flaw detection, penetrant methods, the eddy current technique, ultrasonics, and xeroradiography have been added to the armoury of nondestructive testing. Each of these methods and techniques has its specific field of application. Sometimes a combination of two of them can yield complementary information.

The position today is that there are mandatory requirements for the inspection of welded pressure vessels and for aircraft engines. Nondestructive testing methods have also been applied with great benefit in many other fields of engineering, and yet it would appear as if there were still a large untapped field. It is to be hoped that the author's great skill in giving in simple words a lucid description of the available methods and their scientific background will pave the way to their still wider use. The book is richly illustrated and thus conveys a good idea of the power of the various techniques.

The author is to be congratulated on the meticulous care which he has given to his task. There is hardly a misprint in the whole book (the passage of cathode rays through thin metal foils has been demonstrated by Heinrich Hertz Cp.54); also in *Table I*, one micron should be equal to 10^{-4} cm) and very little over which one would wish to join issue with the author. 'Local temperatures of 1000°C or more' (p. 9) on massive pieces of metal are difficult to accept as experimental facts. The word 'penetrant' has become a generic term and does not always describe a 'liquid of high mobility' even though the liquid may have remarkable searching power.

R. SCHNURMANN

Industrial Design in the United States

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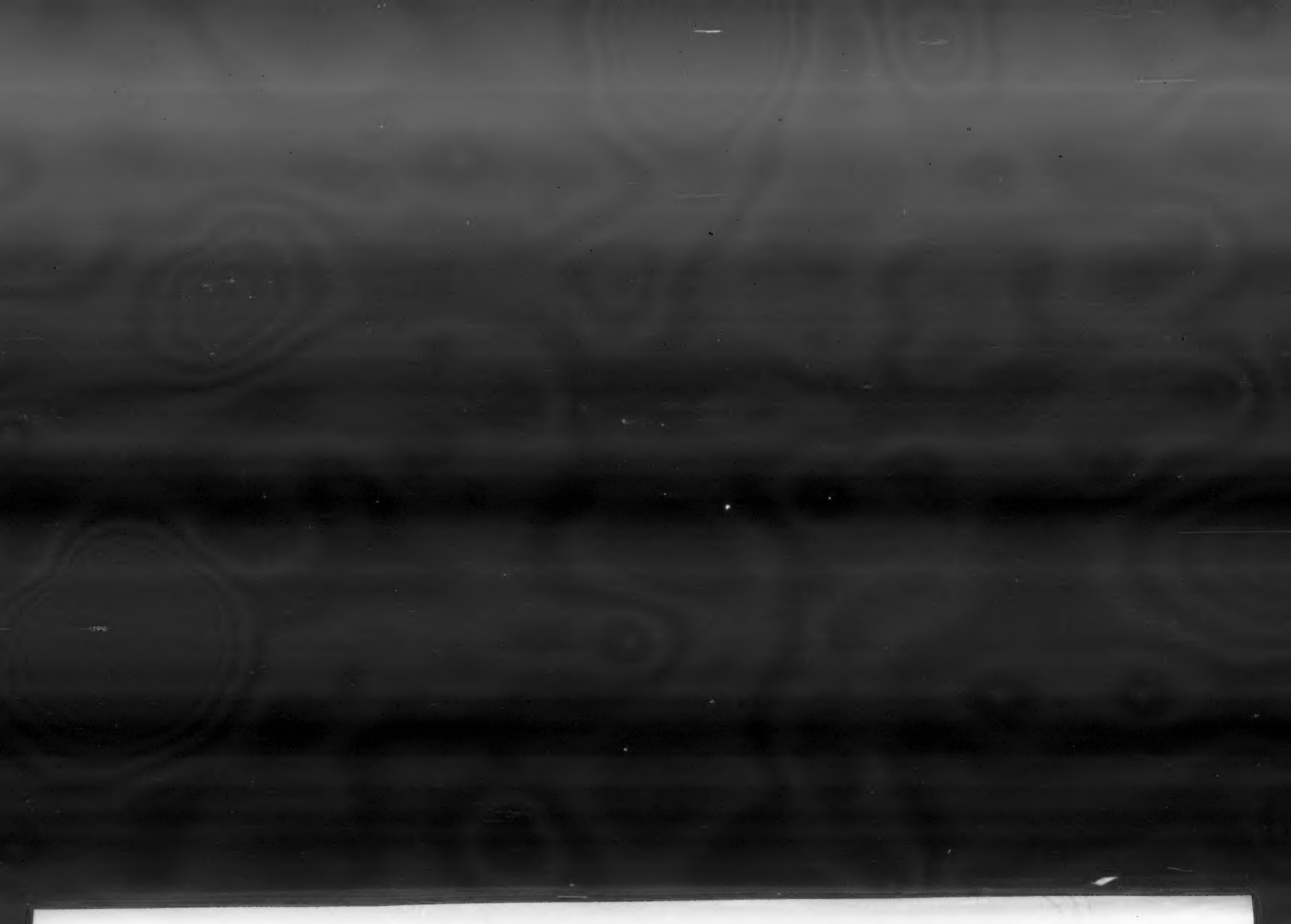
THIS is a report of a mission who visited the United States for two months at the end of 1955 to study 'the function, organization and methods of industrial design in the engineering industries'. Members were drawn from executives in industry, industrial designers and teaching bodies and they represented ten O.E.E.C. countries with one apparent exception: no delegates from the United Kingdom were included. The subjects discussed in the report include definition of the term 'industrial design', organization of design in industrial firms, education in industrial designs and its function, aspects of production design, influence of design on both sales and productivity, *etc.*

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